WASM: Minerals, Energy and Chemical Engineering

Selective Complexation Leaching of Rare Earth Minerals: A New Hydrometallurgical Route Inspired by Geochemical Process

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Doctor of Philosophy

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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

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ABSTRACT

The rare earth elements (REEs) are a subclass of 17 metals from lanthanum to lutetium, yttrium and scandium. The most common rare earth minerals are monazite, xenotime, gadolinite, bastnaesite and allanite.

This present study the potential of organic acids in REEs, specifically in monazite concentrate. Monazite elements from La to Gd, meanwhile xenotime includes elements from Tb to Lu. Currently, hydrometallurgical processes are the only feasible methods to extract rare earth elements (REEs) from monazite and xenotime. Extreme conditions are required such as concentrated lixiviants, high temperatures and corrosive reagents. There have been several attempts to modify methods of extracting REEs from concentrate, but none has been applied on an industrial scale.

The proposed process in this study consisted of a pre-treatment, leaching and hydroxide precipitation stages. It should be noted that each stage worked well in isolation but have not been tested in connection with other stages as a full process. Monazite reacts with the organic acids meanwhile xenotime appears to be less reactive.

The proposed stages for the treatment of monazite concentrate, their vital conditions and characteristics are:

- The first stage consisted of producing RE oxalates by leaching monazite concentrate with oxalic acid. During leaching, dissolved REEs precipitated as RE oxalates and were collected with the solid residue (gangue). Oxalic acid 0.8M, S/L: 0.1, pH 1 for 72 hours are optimal values at 25°C. The residence time can be decreased when the solution is heated to 65°C for 10 hours (0.8M, pH 1, 500 rpm, S/L=0.1), which accelerated the phosphorus release by up to 30% and production of RE oxalates. Further increased of the temperature, increases the dissolution of iron to the detriment of phosphorus. Water quality, S/L ratio, pH and temperature play important roles in the efficiency of this stage. RE oxalate was obtained by conventional method (acid roasting) for comparison with the residue.
- The second stage involved the extraction of the metals from the residue which contains RE oxalate and gangue. During leaching, dissolved REEs are present in the solution. EDTA has great affinity to chelate with metals, Nd, Ce and La have been found in the solution. EDTA 0.8M, S/L: 0.1, pH 10 at 25°C for 5 mins are the optimal values. The pregnant liquor solution (PLS) generated contains far lower impurity levels than conventional processes and there is the potential for a degree of RE selectivity prior to separation. The reaction is very quick (5 mins) which is a great advantage on an industrial process. Water quality, pH and temperature have strong effects in this stage.
- The third stage involved the conversion of RE oxalate EDTA complex in the solution to a RE hydroxide intermediate product suitable for downstream separation and purification processes. The conversion of RE hydroxide (NaOH 2.5M) at 95°C for an hour displayed a crucial point in this process.

The highest recovery in the second stage (almost 60%) was obtained for neodymium. Significant recoveries (>40% of both Ce and La) were obtained for Ce and La and they are the most prolific rare earth elements in the concentrate. Phosphorus and iron are two major concentrate components that are expected to contaminate the leach solution, however they are only present in relatively low concentrations (both less than 100 ppm).

The effectiveness of the system under the conditions tested is highly promising, with reproducible high recoveries of REEs. Moreover, this approach can replace the conventional extraction method without any significant change in the overall current process. It is important to mention that the same separation process, solvent extraction (SX) in most cases, can still be applied as the product fed to SX has been generated from the PLS. In fact, the SX separation process may be simplified if a degree of selectivity can be achieved earlier in the process.

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LIST OF PUBLICATIONS

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- Lazo, D., Dyer L., Alorro, R and Browner, R. 2017. Treatment of monazite by organic acids I: Solution conversion of rare earths. Hydrometallurgy, (174): 202 – 209.
- Lazo, D., Dyer L., Alorro, Richard. 2017. Solubilisation of monazite by organic acids. European Metalurgy Conference (EMC). Leipzig. Germany
- Lazo, D., Dyer L., Alorro, R and Browner, R. 2018.Treatment of monazite by organic acids II: Rare earth dissolution and recovery. Hydrometallurgy, (179): 94 – 99.

STATEMENT OF CONTRIBUTION OF OTHERS

To Whom It May Concern

- I, Daniel Eduardo Lazo, contributed __60%____ to the paper entitled "Silicate, phosphate and carbonate mineral dissolution behaviour in the presence of organic acids: A review."
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  Laurence G. Dyer ____25%_____

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- I, Daniel Eduardo Lazo, contributed ___60%___ to the conference paper entitled "Solubilisation of monazite by organic acids."
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CAT	Computerized axial tomography
EGTA	Ethylene glycol-bis(β-aminoethyl ether)-N,N,N’,N’-tetraacetic acid
DCTA	Diaminocyclohexanetetraacetic acid
DTPA	Diethylenetriaminepentaacetic acid
DPV	Differential pulse voltammetry
ICP-OES	Inductively coupled plasma optical emission spectrometry
IX	Ion exchange
EDTA	Ethylenediaminetetraacetic acid
HEEDTA	Hydroxyethylethylenediaminetriacetic acid
LMWOAs	Low-molecular-weight organic acids
LREE	Light rare earth elements
HREE	Heavy rare earth elements
RE	Rare earth
REEs	Rare earth elements
REO	Rare earth oxides
REY	Rare earth and yttrium
PBM	Planetary ball mill
PLS	Pregnant leaching solutions
S/L	Solid/liquid
SX	Solvent extraction
XRD	X-ray diffraction analysis
XRF	X-ray fluorescence

CHAPTER 1.
INTRODUCTION AND OVERVIEW

The rare earth elements (REEs) have seen much interest in the global market in recent years (Goodenough et al., 2017). They have been identified as "critical" raw material for new technologies (Paulick & Machacek, 2017). REEs cover the lanthanides (from lanthanum to lutetium) including yttrium and scandium (Topp, 1965) (Goodenough et al., 2017). They are typically divided into two groups, the light rare earth elements (LREE or cerium group) from lanthanum to gadolinium and the heavy rare earth elements (HREE or yttrium group) from terbium to lutetium (Jackson & Christiansen, 1993). Scandium is excluded from both groups (LREE and HREE) because of differences based on smaller atomic and trivalent ionic radii compared to those of other REEs (Zhang et al., 2016). Promethium is the only element in this group that is not found in nature but it is created by radioactive decay in nuclear power plants (Balachandran, 2014). REEs with low atomic numbers are more abundant than those with high atomic numbers and the REEs with even atomic numbers are more prolific than REEs with odd atomic numbers (Zhang et al., 2016).

1.1 Geology of rare earth minerals

The rare earths can be found in several deposits: uranium deposits, phosphorites, ion adsorption weathering crusts, paleoplacers, alluvial placer deposits, shoreline placer deposits, deposits hosted by metamorphic rocks, hydrothermal iron-oxide deposits, alkaline igneous complexes, carbonatites, carbonatites with residual enrichment, igneous-affiliated deposits (including pegmatites and veins), and placers of unknown origin (Orris & Grauch, 2002). They can be classified into three categories:

The first group contains the deposits which are currently mined as primary product of REEs:

- Ion adsorption clays
- Placer Deposits
- Carbonatite-related deposits

The second group includes historical production deposits of REEs such as:

- Phosphate rocks
- REE-bearing uranium deposits
- REE-bearing monazite±apatite veins

The third group includes all remaining deposits types (Simandl, 2014).

Australia has several deposits such as residual carbonatite, residual ultramafic, clay lateritic, placers (alluvial, heavy-mineral sands, quartz-pebble conglomerate), etc. There were few exploration projects for REEs in Australia in the last century but in recent years, there has been a boost in exploration due to increasing metal prices. Australia's REE production in the south-west and east have been limited to beach-sand mining where monazite is the main component. Western Australia has carbonatite deposits: Halls Creek Orogen (Cumming range), Yilgarn Craton (Mount Weld, Ponton Creek) and Capricorn Orogen (Yangibana) (Jaireth et al., 2014).

1.2 Rare earth minerals

There are 84 rare earth minerals and 159 potentially rare earth bearing minerals (Orris & Grauch, 2002, Zhang et al., 2016). Nevertheless, only twelve of them have been identified in significant quantities in economic ore deposits: bastnaesite, monazite, xenotime, fluocerite, loparite, polycrase, samarskite, synchysite, aeschynite, gadolinite, fergusonite and parasite (Zhang et al., 2016).

The primary industrial source of LREEs is bastnaesite (the second industrial source is monazite), which contains 67-73% rare earth oxide (REO). The crucial key to obtain bastnaesite concentrate is based on the separation between barium minerals and bastnaesite and calcium minerals. The most important bastnaesite deposits are the Mountain Pass (California, USA) and Baiyun Obo (Inner Mongolia, China) deposits.

The majority of HREEs are obtained from ion-adsorption rare earth clay (the second industrial source is xenotime), which was first discovered in China's Jianxi Province in 1969 (Zhang et al., 2016). Ion-adsorbing clay mineral, where REEs are adsorbed as ions on the surface of the clays, can have HREEs making up to 60% of the REO content (including yttrium). Quartz, clay minerals and other rock-forming minerals are the most important components of ion-adsorbing clay mineral. In the ion-adsorbing clay mineral, REEs are not capable of being hydrolyzed or being dissolved in pure water, however, they follow the ion exchange laws and can be easily separated by leaching, precipitation and calcination (Zhang et al., 2016).

In 2017, the global proven total rare earth oxide (TREO) reserves reached approximately 120 Mt distributed primarily among China, Brazil, Vietnam and Russia with reserves of 44 Mt, 22 Mt, 22 Mt and 18 Mt, respectively (USGS, 2017).

1.3 Rare earth elements (REEs)

The term REEs refers to a group of 17 metallic elements, covering the lanthanide series coupled with the chemically similar yttrium and scandium (Gupta & Krishnamurthy, 2005). Scandium and yttrium are categorised as REEs as they are considered precursors of this series (Topp, 1965). These elements are generally classified into two sub-groups, the light rare earth elements (LREEs) or cerium group (lanthanum to gadolinium) and the heavy rare earth elements (HREEs) or yttrium group (yttrium, terbium to lutetium) (Simandl, 2014). All REEs can be found stable in nature except for promethium which is produced by radioactive decay (Balachandran, 2014). Scandium has significantly different properties from the lanthanides, therefore, although it is not included in either the LREE or HREE classifications (Simandl, 2014).

With the exception of scandium, individual rare earths do not naturally occur, and they are found as mixtures with varied ratios (Spedding, 1978). The most common rare earth minerals are xenotime, monazite, allanite, bastnaesite, and gadolinite (Panda et al., 2013) (compositions given in Table 1.1). Only three of these minerals (bastnaesite, monazite, and xenotime) have been exploited on a commercial scale (Jordens et al., 2013). Bastnaesite, which can contain U or Th, has become the primary ore mineral source of LREEs (Voncken, 2016).

Table 1.1: Composition of major rare earth-bearing minerals

Mineral	Composition
Monazite	$(Ce, La, Y)PO_4$
Bastnaesite	$(Ce, La, Y)FCO_3$
Allanite	$(Ca, Ca, La, Y)_2(Al, Fe^{3+})_3(SiO_4)_3(OH)$
Gadolinite	$(Ce, La, Nd, Y)_2FeBe_2(SiO_4)_2O_2$
Xenotime	YPO_4

1.4 Applications of the REEs

The applications of REEs cover many areas of industry, mainly glass additives, phosphors, automobile catalysts, magnets, battery alloys, fluid catalytic cracking and metallurgy oxide batteries (Kumar et al., 2014). REEs are used in critical defense applications: communication systems, anti-missile defense systems, jet fighter engines and missile guidance systems. Colour TV and other display systems use red phosphor which needs to be produced using high purity oxides (more than 99.99%) of terbium, europium and yttrium. Rare earth permanent magnets (Sm-Co alloys and Nd-Fe-B alloys) have a significantly better performance that those of traditional magnets leading to applications in energy generation. The addition of REEs aids to purify molten metal or alloy by removing harmful impurities (sulphur and oxygen), changing the distribution and configuration of impurities, making the grains finer and decreasing the amount and size of inclusions (Zhang et al., 2016). Increasing the capacity of petroleum cracking units between 20-30% and increasing gasoline conversion by 10% can be achieved by adding REEs to fluid cracking catalysts. Several applications of REEs, due to chemical reactivity and crystal structures, include polishing, decolouring/colouring, glass clarification and ceramic pigments. Y is broadly used in alloys, medical devices, superconductors, lasers and garnets. Pr is employed in aircraft engine alloys, fiber optics, computerized axial tomography (CAT) scan machines and permanent magnets (Zhang et al., 2016).

REEs have an important role in the production of super alloys, medicines, catalysts, and permanent magnets among other advanced applications. The magnetic and spectroscopic properties of REEs have a crucial importance in many areas of new technologies from mobile phones to satellite systems (Kumar et al., 2014).

1.5. Chemistry of REEs

1.5.1 Electronic Configuration: The unique nature of rare-earth metal chemistry is mainly the result of an uncommon electronic configuration. They display essentially unique properties, which influence their ionic bonding via atomic size and ionic charge (Moeller, 1971). Moving along the 4^{th} and 5^{th} periods (those containing scandium and yttrium) additional electrons occupy the 3d and 4d orbitals respectively. Conversely in the lanthanide series (lanthanum to lutetium), these additional electrons are added to the inner and well-shielded 4f orbital rather than to 5d (Table 1.2). Furthermore, there is a well-known propensity of the electron to drop from 5d to 4f level (Moeller, 1971). Experimental results indicated that some similarities

among the chemical properties of the elements is the outcome of strikingly similar electronic configurations (Gupta & Krishnamurthy, 2005).

Although the 4f electrons do not have strong influence in valence forces which define the chemical properties of REEs, they can have an important role in several physical properties. Most of the lanthanide elements are strongly paramagnetic their spin and orbital angular momentum are not equally balanced (Spedding, 1978).

Table 1.2: Electronic configurations of atoms, derived tripositive ions and oxidation states, adapted from Moeller (1971).

		Outermost Electronic Configuration		
Element	Atomic Number	Idealized	Probable	Oxidation States
Sc	21	$3d^14s^2$	$3d^14s^2$	3
Y	39	$4d^15s^2$	$4d^15s^2$	3
La	57	$5d^16s^2$	$5d^16s^2$	3
Ce	58	$4f^15d^16s^2$	$4f^26s^2$	3,4
Pr	59	$4f^25d^16s^2$	$4f^36s^2$	3,4
Nd	60	$4f^35d^16s^2$	$4f^46s^2$	3
Pm	61	$4f^45d^16s^2$	$4f^56s^2$	3
Sm	62	$4f^55d^16s^2$	$4f^66s^2$	2,3
Eu	63	$4f^65d^16s^2$	$4f^76s^2$	2,3
Gd	64	$4f^75d^16s^2$	$4f^75d^16s^2$	3
Tb	65	$4f^85d^16s^2$	$4f^96s^2$	3,4
Dy	66	$4f^95d^16s^2$	$4f^{10}6s^2$	3
Ho	67	$4f^{10}5d^16s^2$	$4f^{11}6s^2$	3
Er	68	$4f^{11}5d^16s^2$	$4f^{12}6s^2$	3
Tm	69	$4f^{12}5d^16s^2$	$4f^{13}6s^2$	2,3
Yb	70	$4f^{13}5d^16s^2$	$4f^{14}6s^2$	2,3
Lu	71	$4f^{14}5d^16s^2$	$4f^{14}5d^16s^2$	3

1.5.2 Oxidation State: The significant correlation in valency configuration in REEs and almost similar energies of the 6s, 5d and certain 4f electrons leads to almost identical oxidation stated for all rare earths. Under most natural conditions, all REEs have a common (3+) oxidation state, with uncommon behaviour under certain circumstances, predominantly seen in Ce^{4+} and Eu^{2+} (Haskin & Paster, 1978). The chemistry of the lanthanides is mainly ionic and is influenced predominantly by the size of the M^{3+} ion (Topp 1965, Gupta & Krishnamurthy 2005). REEs are hydrolysates because the trivalent (divalent for europium and tetravalent for cerium) ions easily experience hydrolysis in aqueous solutions (Dubinin, 2004).

1.5.3 Lanthanide Contraction: The lanthanide series displays an odd behavior, in which the size of the atoms and ions decrease more than expected with increasing atomic number. The additional 4f electrons provide very weak shielding to the outer valence electrons increasing the effect of the additional nuclear charge (Gupta & Krishnamurthy, 2005). This contraction opposes the trends across the rest of the periodic table because there is no other sequence of elements for which 14 electrons are consecutively added to the electronic shells without

playing a role in chemical bonding (Topp, 1965). While the similarity in chemical bonding presents difficulties in separating the lanthanides, the contraction provides some assistance.

1.5.4 Basicity: Basicity is a measure of reactivity of a metallic element, primarily with regards to the ease with which electrons are lost or a lack of attraction of an ion for electrons (Moeller, 1971). Basicity is a very important property of REEs and is related to the ionic size and thus lanthanide contraction (Gupta & Krishnamurthy, 2005). Basicity has been used to explain several phenomena, covering the degree to which cations hydrolyze in aqueous solution, the relative solubilities of salts of all forms, the ability to decompose salts (containing oxyanions) by heat, and the stabilities of complex ions (Moeller, 1971). This property determines the base for the fractionation method to separate individual REEs (Moeller, 1971).

1.6 Demand for REEs

The demand for REEs has had a substantial increase from 75,500 tonnes (t) of rare earth oxide (REO) in 2000 to 123,100 t of REO in 2016 (Roskill, 2016). Their use in NdFeB magnets, wind turbines, erbium-doped glass for communications and specifically hybrid and electric vehicles is expected to drive future demand to 2026 (Goodenough et al., 2017). The global production of REO annually rose from 60,000 t in 1994 (Paulick & Machacek, 2017) to 126,000 t in 2016 (USGS, 2017). The increase in the price of raw material commodities (copper, iron or gold) encourages exploration due to the value displayed by newly discovered deposits. However, the REE scenario is different because any new mine site project needs to compete with REE mining in China that has a near-monopoly of production and vertical integration of the value chain (mining, beneficiation, manufacturing, assembly, and final products) (Paulick & Machacek, 2017). Furthermore, several advantages of Chinese REE producers such as government support, easy environmental regulations and cheap labor have a great impact on non-Chinese REEs companies (Folger, 2011). During the 1980s, 1990s and 2000s, mineral processing research related of rare earth minerals was scarce (Goodenough et al., 2017).

1.7 Current technologies of extraction

The conventional methods used to extract REEs depend on the type and grade of minerals in the ore and the intended products (Zhang & Edwards, 2013; Jha et al., 2016). The current technologies for solubilising rare earth minerals employ pretreatment (roasting or cracking), corrosive reagents (sulphuric acid), highly concentrated reagents (i.e. 98% H_2SO_4), high temperatures (> 200°C) (Franken, 1995) and often produce hazardous by-products (sulphur dioxide, silicon tetrafluoride, and toxic and radioactive tailings) (Zhang & Edwards, 2013). Several ore beneficiation techniques are used to concentrate rare earth minerals to make rare earth projects economically viable (Zhang et al., 2016).

Rare earth mineral processing is comprised of two primary operation phases. First, physical processing involves crushing and grinding followed by beneficiation, which separates the REE-bearing minerals from much of the gangue to produce a concentrate. Aside from ion-adsorbed clays (Southern China) and heavy mineral sands deposits, almost all rare earth deposits need some degree of comminution before separation and this process is reliant on slurried feed material (Jordens et al., 2013). Gravity, electrostatic, magnetic and flotation separation techniques are used to beneficiate ores. Flotation is the common method of beneficiation in rare earth processing where the fine liberation size is achieved (Zhang et al., 2016).

1.7.1 Physical processing and beneficiation

1.7.1.1 Bastnaesite

Bastnaesite ore commonly contains other minerals (quartz, feldspar, calcite, etc.), which have similar beneficiation properties (specific gravity, magnetic susceptibility, floatability and electrical conductivity) making the concentration process a challenging task. Figure 1.1 shows the Mountain Pass flowsheet of production to obtain bastnaesite concentrate by flotation. The ore is ground to below 100 mesh and sent to agitated tanks (four stages). The temperature of the slurry is raised to 60°C by injecting steam in the first tank. A pH of 8.95 is set by adding soda ash. In the second stage, the temperature is increased to 80°C (employing steam) and Orzan (a kind of lignin sulfonate) is added in as a depressant. The temperature of the slurry is raised to boiling in the third stage and N-80 oleic acid is added as a collector. The slurry is cooled down to 60°C in the fourth stage. Mountain Pass achieved 60% REO concentrate by using this flowsheet with one tank for rougher flotation, four tanks for cleaner flotation and one tank for scavenger flotation (Zhang et al., 2016).

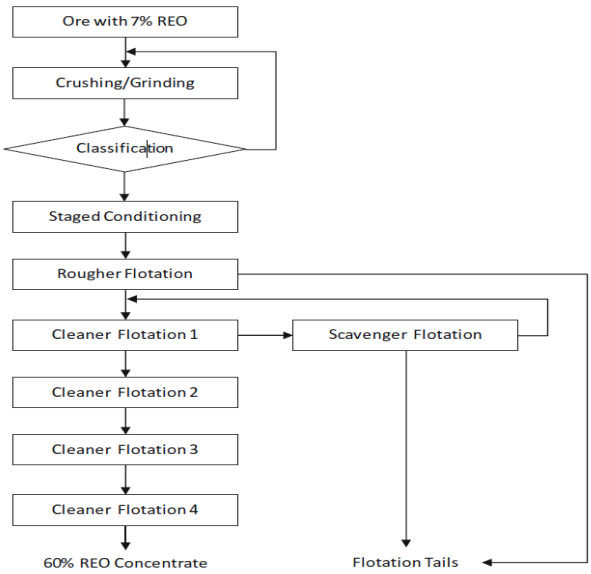

Figure 1.1: Flowsheet for the production of bastnaesite concentrate at Mountain Pass (Zhang et al., 2016)

1.7.1.2 Monazite

Monazite was the first source of REEs processed on an industrial scale and is an important source of LREEs (Zhang et al., 2016) along with bastnaesite. Monazite is commonly concentrated by high-capacity gravity separation stages, particularly from mineral sands, due to its high specific gravity of 5, whereas, the common gangue associated with these deposits has a specific gravity of 3.5 (Jordens et al., 2013).

At Mt Weld which is a carbonatite deposit the common gangue minerals are alumosilicates, phosphates, haematite and Fe-hydroxides and about 50% of the monazite is contained in the minus 25µm fines. This ore is amenable to concentration by desliming and flotation (Bulatovic, 2010).

Figure 1.2 shows the Mt Weld flowsheet for grinding and desliming. Three stages are required with a feed pulp density of 15%. Figure 1.3 shows the Mt Weld flowsheet for the flotation stage which is conducted with a pulp density of about 60%. Cationic collectors (i.e. oleic acid

and sodium oleate) are employed to float the monazite in the pH region of 7 – 11 (Bulatovic, 2010). Monazite recovery is strongly affected by Na_2S-$9H_2O$ added into the rougher and cleaner stages (Bulatovic, 2010).

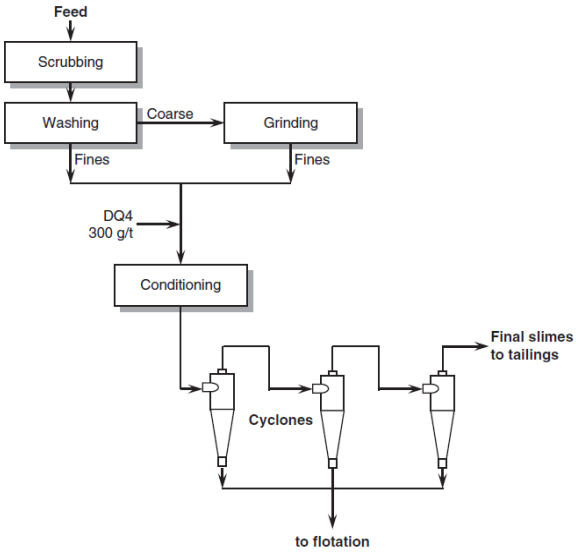

Figure 1.2: Flowsheet for grinding and desliming monazite concentrate, Mt Weld (Bulatovic, 2010)

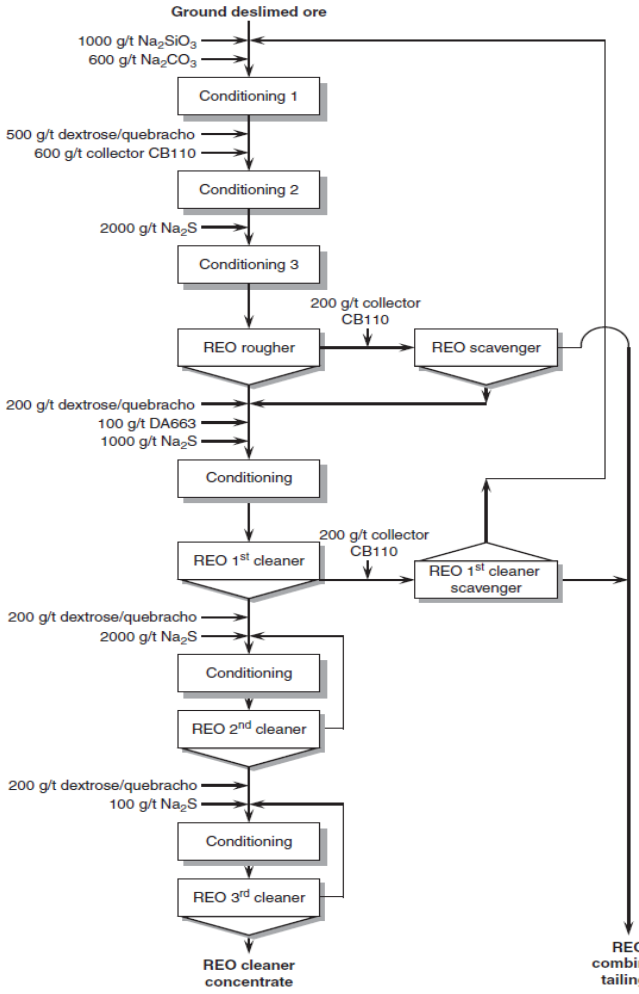

Figure 1.3: Flowsheet for flotation of monazite concentrate, Mt Weld

(Bulatovic, 2010)

1.7.1.3 Xenotime

Xenotime, along with ion-adsorbing clay, are the most important sources of HREEs (Jordens et al., 2013). Strong magnetic separation, electrostatic separation and gravity separation are used alone (or in combination) to achieve separation of xenotime, but there are some difficulties separating fine-grained ores. Therefore, flotation is employed for the case of fine grains (Zhang et al., 2016).

Figure 1.4 described xenotime beneficiation process for coastal placer deposit, SE China. After the third stage (double rotors magnetic separation), the main elements are classified and take different routes according to their properties. Limonite, magnetite and ilmenite followed the same process of separation which involved electromagnetic and magnetic separation. Xenotime concentrate involved flotation, shaking table, electromagnetic and magnetic separation. Zircon was separated from Leucoxene and Rutile employing shaking table. Then, zircon separation from impurities involved magnetic and electromagnetic separation. Leucoxene and rutile followed almost the same route of separation which involved shaking table, flotation, electromagnetic and magnetic separation where in this last stage, they were finally separated.

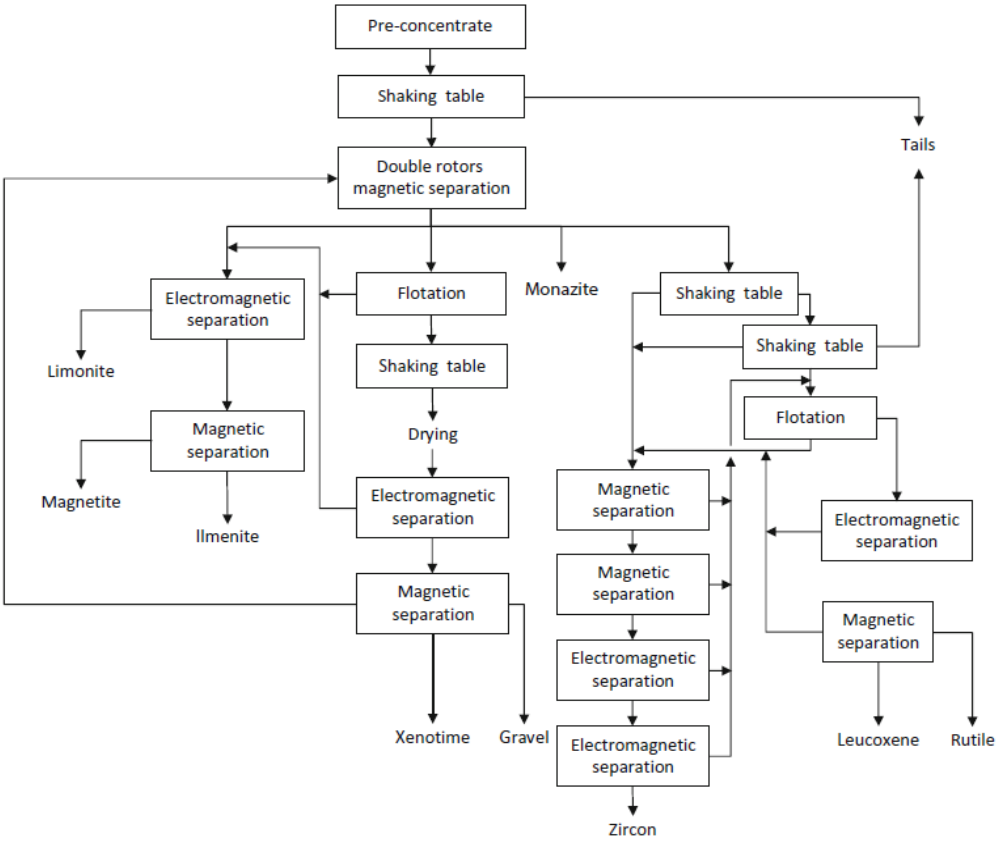

Figure 1.4: Xenotime beneficiation process (from coastal placer deposit, SE China)

(Zhang et al., 2016)

1.7.2 Chemical process of extraction of REEs

Chemical processing, which covers extraction and the recovery, initially transforms the relevant concentrate minerals to more soluble compounds to prepare them for subsequent leaching. This is followed by purification and separation, the latter of which is very difficult because of the chemical similarities of the rare earth (Zhang & Edwards, 2013).

Most of the current technologies for REE extraction are conducted by hydrometallurgical methods. The major conventional hydrometallurgical processes for the primary rare earth minerals of interest (monazite, bastnaesite and xenotime) are well described in the literature (Habashi 1997, Gupta & Krishnamurthy, 2005). After obtaining the concentrate, the chemical process follows two main methods: alkaline attack by NaOH or acidic attack by H_2SO_4 (direct leaching with H_2SO_4 or acid roasting with H_2SO_4 and the product leached with water).

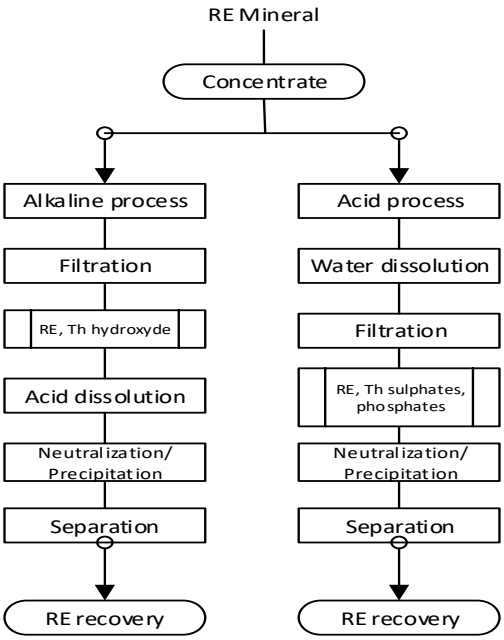

Figure 1.5: Primary hydrometallurgical recovery processes of REEs, adapted from Kim and Osseo-Asare (2012)

The description of the extraction of rare earth elements as shown in Fig. 1.5 are discussed below where only direct leaching and acid roasting are mentioned. Acid roasting is described in more detail because it will be used to obtain RE oxalate and RE hydroxide for comparison in XRD analysis.

1.7.2.1 Direct leaching with H_2SO_4: This process is described by Barghusen & Smutz, (1958) (Fig. 1.6) and involves the leaching of the concentrate with sulphuric acid (98%) at high temperature (210°C) for 4 hours in a high-pressure vessel. Subsequent, the generated solution is diluted by adding deionized water. The pH in the PLS was increased to 1.5 by adding ammonium hydroxide. Oxalic acid is added to the solution to precipitate the REEs with the creation of RE oxalate.

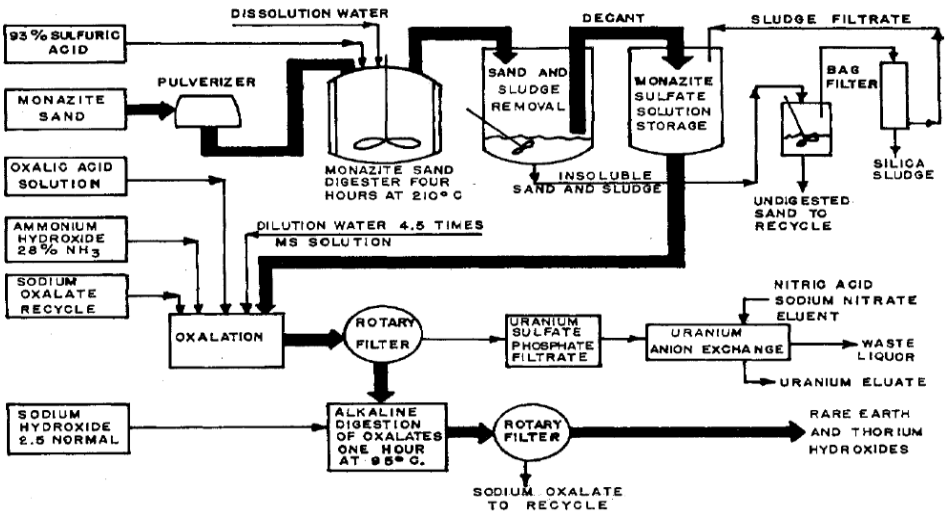

Figure 1.6: Flowsheet for obtaining RE hydroxides using direct leaching with H_2SO_4 for monazite concentrate (Barghusen & Smutz, 1958)

1.7.2.2 Acid roasting with H_2SO_4

It basically involves the mixture of the concentrate with H_2SO_4 and heating to about 210°C for 4 hours, Subsequent, the grey colored mud is leached with water. Acid roasting can be used with monazite (Kim & Osseo-Asare, 2012), bastnaesite (Zhang et al., 2016) or xenotime (Sadri et al., 2017) concentrate.

Acid roasting can be classified into high temperature roasting (> 300°C) and low temperature roasting (< 300°C) (Shi, 2009; Zhang & Edwards, 2013). During the 1970s, the low temperature process was developed to treat low grades concentrates, whereas during the 1980s, the high temperature process was invented to treat high grade concentrates and avoid the creation of soluble impurities (Shi, 2009; Zhang & Edwards, 2013). The decomposition rate is reduced using higher temperature (> 300°C) whereas leachable thorium is also decreased by the creation of insoluble ThP_2O_7 (Zhang & Edwards, 2013; Zhang et al., 2016).For low temperature roasting of monazite, a concentrate is combined with 98% sulphuric acid (solid-liquid mass ratio ~1:1) at 200 to 230°C, for 4 hours. This process converts the rare earth phosphate minerals (in our study, monazite concentrate) to sulphate compounds, (Equation 1.1), that are far easier to dissolve. Furthermore, Th reacts with the sulphuric acid and this created a more amenable compound as seen in Equation 1.2. The product is a grey-colored metal sulphate solid (Kim & Osseo-Asare, 2012).

The high temperature acid roasting process is simple but produces hazardous gases such as sulphur dioxide (SO_2) and sulphur trioxide (SO_3). It is common to place a water scrubber to clean most of the exhaust gases. A second scrubber is used to purify the exhaust gases before they are released to the atmosphere, adding further expense (Zhang & Edwards, 2013).

Subsequent to acid roasting, 4.5 parts by volume of water was added to the roast product to solubilize the rare earth sulphate and which leaves a residue containing zircon, rutile ilmenite, silica, and undigested monazite (Sadri et al., 2017). The pH in the PLS was increased to 1.5 by adding ammonium hydroxide. To separate the REEs from other soluble impurities, selective precipitation is employed. REEs and Th are precipitated by the addition of oxalic acid which create RE oxalate and separate from sulphate and phosphate ions which could jeopardize the subsequent liquid separation (Zhang & Edwards, 2013).

$$2REPO_{4(s)} + 3H_2SO_4 \xrightarrow{yields} (RE)_2(SO_4)_{3(s)} + 6H^+ + 2PO_4^{3-} \quad \text{.....(1.1)}$$

$$Th_3(PO_4)_{4(S)} + 6H_2SO_4 \xrightarrow{yields} 3Th(SO_4)_{2(s)} + 12H^+ + 4PO_4^{3-} \quad \text{.....(1.2)}$$

Both processes require inert linings to protect the processing equipment (Franken, 1995). Sulphuric acid (H_2SO_4) is the major raw material for an acid roasting and direct leaching processes. The type of material for the vessel for sulphuric acid depends on tank size, temperature, costs, acid concentration and desired acid quality (Knowledge for the sulphuric acid industry website). The 98% concentration sulphuric acid contains a small amount of free water. The presence or otherwise of passive surface films of chromium oxide determined the behavior of a stainless-steel tank under the effect of sulphuric acid (Richardson, 2010). Tantalum inert lining is the most adequate corrosion protection under 98% concentration H_2SO_4 and 210°C for four hours and has a high price tag (Extreme bolt & fastener website).

1.7.2.3 Alkali Treatment

Alkali treatment is employed for monazite and xenotime processing, but it is not suitable for bastnaesite as the reagent consumption is too high (Sadri et al., 2017). Alkali treatment is carried out in autoclaves (alkali concentration ~60%, solid-liquid mass ratio ~1:1) at high temperature (~150°C) (Kim & Osseo-Asare, 2012; Sadri et al., 2017) and agitated for 4 hours (Franken, 1995). Trisodium phosphate (Na_3PO_4) is retrieved as a by-product (fertilizer) after the filtration stage (Sadri et al., 2017). The conversion reactions are given by Equations 1.3 and 1.4 (Kim & Osseo-Asare, 2012).

$$RE(PO_4)_{(s)} + 3NaOH \xrightarrow{yields} RE(OH)_{3(s)} + 3Na^+ + PO_4^{3-} \quad \text{.....(1.3)}$$

$$Th_3(PO_4)_{4(s)} + 12NaOH \xrightarrow{yields} 3Th(OH)_{4(s)} + 12Na^+ + 4PO_4^{3-} \quad \text{.....(1.4)}$$

After the REE hydroxide is generated and precipitated various acids, such as HNO_3, H_2SO_4, and HCl, may be used to dissolve the hydroxide product (Kim & Osseo-Asare, 2012; Sadri et al., 2017). The selection of the acid depends on the intended separation process (Kim & Osseo-Asare, 2012; Sadri et al., 2017). Alkaline treatment has several advantages: it performs the simultaneous removal of phosphorus, the creation of useful sodium phosphate (fertilizer) and regeneration of alkali (Abdel-Rheim, 2002, Kumar et al., 2014). The great disadvantage of this method is the creation of RE compounds fused with NaOH which are difficult to dissolve (Zhang & Edwards, 2013; Zhang et al., 2016).

1.7.3 RE hydroxide precipitation

After obtaining RE oxalate in both processes (direct leaching and acid roasting with H_2SO_4), the residue is digested with sodium hydroxide (2.5 M) and heated for an hour at 95°C. The digested solution is filtered, and the residue is RE hydroxide. The RE hydroxide cake is calcinated at 500°C for 1 hour where the cerium is converted to the higher valence. The calcined hydroxide is dissolved in nitric acid and tributyl phosphate (TBP) used for liquid – liquid (SX) extraction (Barghusen & Smutz, 1958) (Fig. 1.7). More detail explanation of separation methods is in Section 1.8.

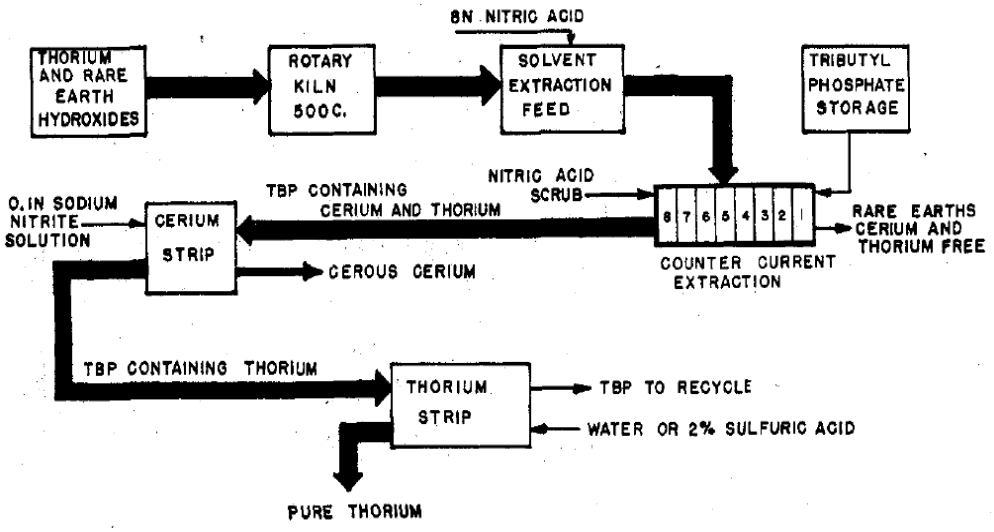

Figure 1.7: Separation of REEs using solvent extraction (Barghusen & Smutz, 1958)

1.8 Mechanochemical treatment

To enhance alternative extraction techniques, mechanochemical treatment has been investigated. Mechanochemical is a treatment which employs mechanical energy, often applied by milling, to initiate structural transformation and chemical reactions (McCormick & Froes, 1998). Juhasz, A. (1974) suggested that two main processes occurred during mechanochemical treatment. The primary process improves the reactivity of minerals (increase the surface area, increase surface energy). The secondary process (recrystallization, adsorption, aggregation) occurred quickly in activated systems and may happen during milling or after milling. Comminution of mineral grains is the main result of mechanical activation where there are a great number of changes of the physicochemical properties (Baláž, 2003).

Many interesting applications (such as creation of advanced materials with new microstructures, waste processing and improved mechanical properties) have been achieved employing activation by mechanochemical treatment (McCormick & Froes, 1998). Mechanochemical treatment was used in earliest applications for mechanical activation. By ultrafine grinding of minerals, i.e. chalcopyrite or sphalerite, the chemical reactivity was increased. Therefore, the minerals can be leached under less aggressive conditions (McCormick & Froes, 1998). Planetary, vibratory, attritor ball mills, etc. (Fig. 1.8) are the most common instruments where mechanochemical treatment is performed (Wiecczorek-Ciurova & Gamrat, 2007).

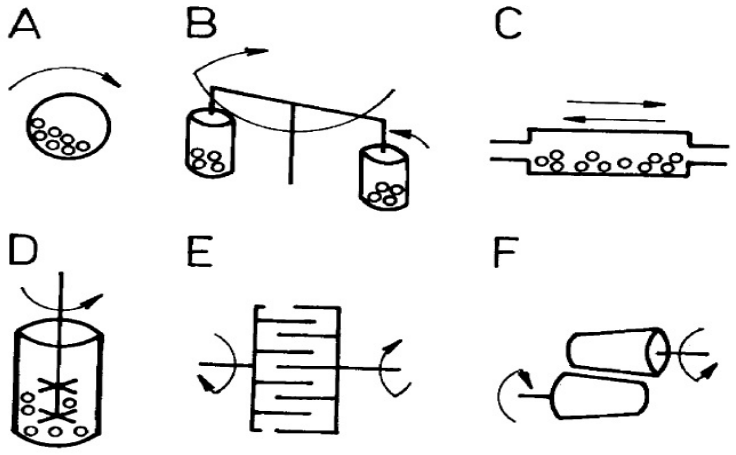

Figure 1.8: Types of mills for mechanochemical treatment: A, ball mill; B, planetary mill; C, vibratory mill; D, stirring ball mill (attritor);E, pin mill; F, rolling mill (Boldyrev, 1986).

Kim et al., (2009) investigated mechanochemical treatment by milling sodium hydroxide and monazite and subsequent leaching using sulphuric acid for the extraction of REEs. Monazite concentrate was mixed with NaOH in a stoichiometric rate of 1.67:1. Then, 4 g was added in a 50 cm^3 planetary ball mill (Fristch Pulverisset-7) with 7 zirconia balls (15 mm diameter) in air at a constant speed of 650 rpm with several milling time durations from 15 mins to 240 min tested. More compacted bodies are observed when milling time increases to 30 mins and 60 mins due to many small particles are welded together (reaction milling). Figure 1.9 shows the XRD graphs under different milling time. It can be observed how the phase gradually changed from monazite to new phases as milling time increases (activation milling).

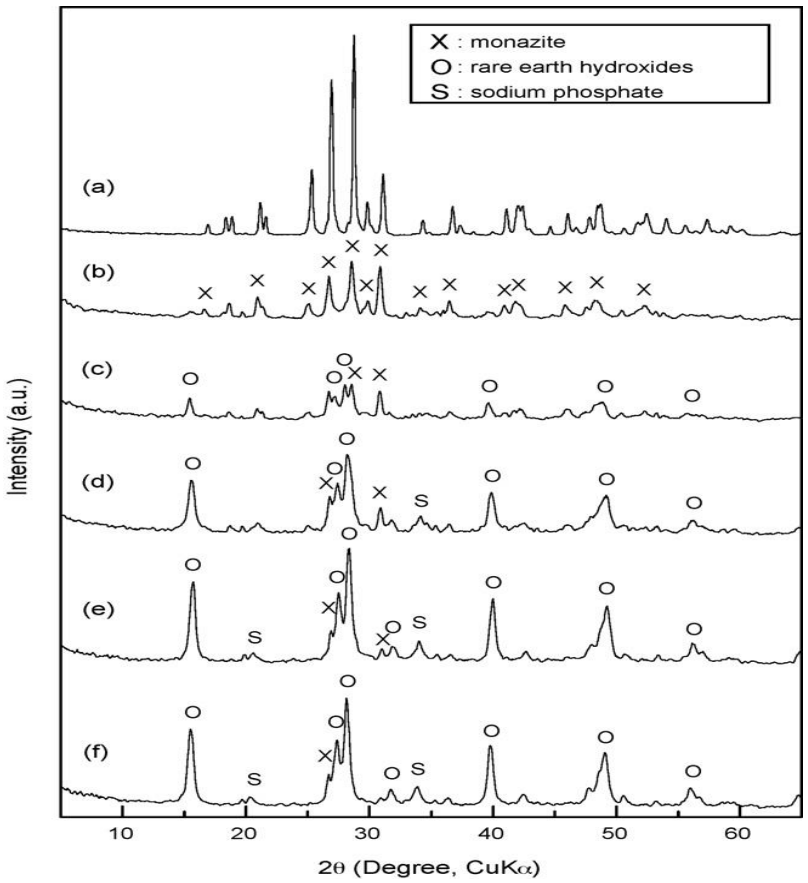

Figure 1.9: X-ray diffractograms of a mixture of NaOH, monazite and milled (a) 0 min (concentrate) (b) 15 min (c) 30 min (d) 60 min (e) 120 min and (f) 240 min (Kim et al., 2009).

At the end of the milling process, the milled powder was washed with distilled water with energetic agitation for 30 min. The solution was filtered, and the residue placed in an oven at 80°C for 24 hours. The dried powder was leached with H_2SO_4 at room temperature. La, Nd and Sm extraction yield was increased by 85% (powder milled for 120 min) under the effect of 0.05 N H_2SO_4 solution. As the milling times increases, the Ce and Pr yield extraction increases. Therefore, the recovery of REEs increased as the milling time was increased from the milled powder at room temperature (Kim et al., 2009).

1.9 Separation of REEs

There are three general methods available for separating rare earth elements according to Spedding (1978), fractional crystallization, solvent extraction and ion-exchange. Vocken, J. (2016) defines fractional crystallization as "a part of a salt in solution is precipitated by a change in temperature or by evaporation of the saturated solution." During fractional crystallization, the difference between adjacent rare earths are frequently so small that many repetitions are required to achieve significant separation (Healy & Kremers, 1971).

Vocken, J. (2016) defines solvent extraction SX (also called liquid- liquid separation) as "SX is the transfer of one or more solutes contained in a feed solution to another, essentially immiscible liquid (solvent)." Ambient temperatures and pressures are needed to perform SX with aqueous and organic solutions (Kislik, 2012). Liquid-liquid separation (solvent extraction) has shown that despite their chemical similarity, solvent extraction is able to effectively separate the REEs, however it requires a great number of stages (> 100 in some cases) (Peppard, 1971).

Vocken, J. (2016) defines ion exchange as “This method involves the exchange of ions between electrolyte solution and a usually solid material called an ion exchanger.”. The fractional crystallization is not explained in detail due to economical unrealistic approach. SX is explained in detail because is the most common method used for separation on industrial scale.

1.9.1 Ion exchange (IX)

Kleber & Love (1963) defined “An ion exchange resin or ion exchanger can be considered as an ionic salt in which one of the ions is attached to an insoluble organic matrix”. In a cation exchanger, the ion charge is positive. Similarly, the ion charge is negative in an anion exchanger or anion exchanger resin. During the contact between salt solution and ion exchanger resin, the displacement of the mobile ion in the resin may be occurred by 1) larger ion radius displaces smaller ion radius when two ions have similar charged ions 2) an ion of lower charge was displaced by an ion of higher charge 3) the law of mass actions applied for displacement (Gupta & Krishnamurthy, 2005).

It was discovered that individual rare earths moved down in a column at different speed and each element can have different affinities with the resin under the effect of the eluent without altering the equilibrium of other elements created (Fig. 1.10) (Powell, 1971).

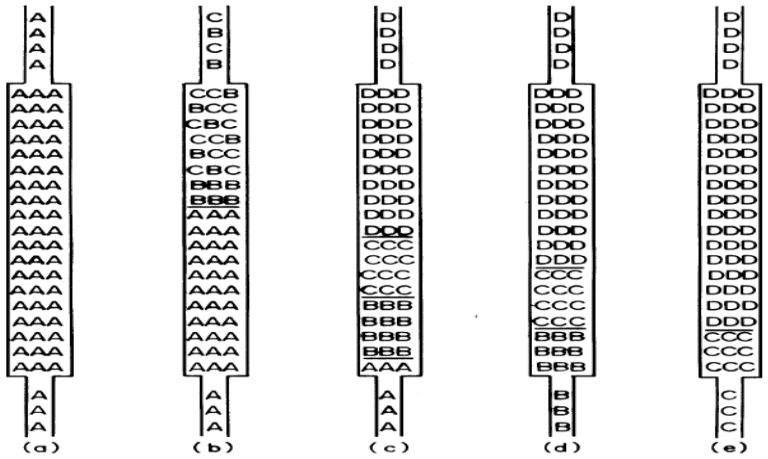

Figure 1.10: Simple displacement of the ions in columns for displacement chromatography a) A ions b) B and C ions where C has stronger affinity with the resin than B c) eluant containing D ions has stronger affinity to the resin than A, B and C ions d) B ions travelling through columns e) C ions travelling through column(Powel, 1971)

1.9.1.1 Ion exchange separation in the Manhattan project

During a meeting of the American Chemical Society on September 17, 1947 in NY, USA, there was symposium of Ion Exchange Separation where most of the research papers described the process for separation of REEs and other fission products as part of the Manhattan Project conducted during and after World War II. The separation of REEs has been identified as a great challenge and many scientists have worked for years employing fractional crystallization processes to produce high purity REEs. The development of the Manhattan Project involved many researchers and workers from different areas and laboratories working together. At the

start of the Manhattan Project, synthetic organic exchange resins (Amberlite IR-1 and IR-4 resins) were able to adsorb several products of the fission of uranium. These ions can be eluted from the resins by several reagents under defined parameters (Warren et al, 1947).

From the finding of Boy's group (Warren et al, 1947), they thought that the fission products could be separated from each other by using the Amberlite resins. They focused their interest on fission products such as zirconium, the REEs, iodine, tellurium, columbium, yttrium, strontium, and barium. Dr. Spedding (Iowa State College) though that these resins might separate the REEs in huge quantities. A research group was formed to investigate this option and was started at Iowa State College in December 1944. (Warren et al., 1947). The ammonium citrate solution was used as an eluant for the rare earths from a column of Amberlite resin. The equilibrium constants among RE citrate complexes are slightly different, therefore, the speed of moving down through the column differ enough to allow separation (Spedding et al., 1947). Then, it was replaced by the more effective EDTA (Cotton, 2006). Several other organic acids such as tartaric, lactic and ethyl acetoacetate may create also proved to be useful complexing agents (Tompkins & Mayer, 1947). It appears that cost/recovery was the primary reason that citric acid and EDTA were the eluents of choice.

1.9.2 Solvent Extraction (SX)

SX is the most common process used to separate REEs in an industrial scale. Figure 1.11 shows a vessel where one of the liquids is water and the other one generally is an organic solvent (Rydberg et al., 2004).

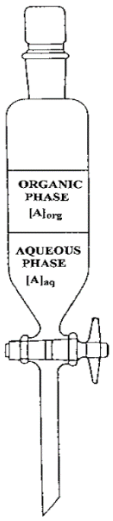

Figure 1.11: Solvent extraction distribution. A solute, organic solvent (upper layer) and aqueous phase (lower layer) (Rydberg et al., 2004)

A simple SX system can be seen in Figure 1.12 where the solvent and metal-bearing aqueous solutions are fed in a counter-current system and has three stages which are extraction, scrubbing and stripping. Thus, during extraction stage, the metal ions to be separated are moving to the organic phase (from the aqueous phase). After the extraction stage, the loaded solvent with metals (or impurities) goes to another stage where it is scrubbed (removing the metals) with an appropriate aqueous solution. From the scrubbing stage, the loaded solvent with metals from the organic phase is stripped by employing some appropriate aqueous solution (Ritcey, 2006).

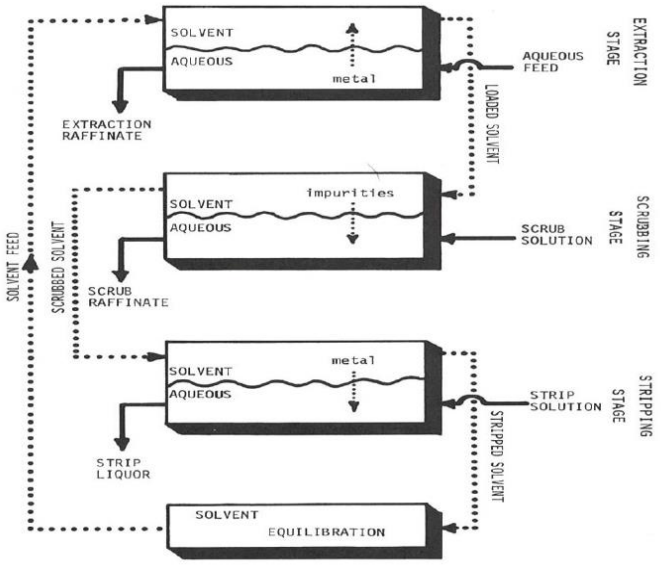

Figure 1.12: A general solvent extraction (SX) circuit (Ritcey, 2006)

Kinetic process is the fundamental principle of solvent extraction. The factors which determine the rate of extraction are: a) interfacial region resistances b) interfacial area where mass can be transferred c) the driving force (displacement from equilibrium). There has not been any improvement for a long time. Therefore, the industry must be assured that the time of contact is long enough to achieve equilibrium or recognize the inefficiency of a single stage and use more stages. Figure 1.13 displays how the equilibrium in SX diminishes when there are inefficiencies (Rydberg et al., 2004).

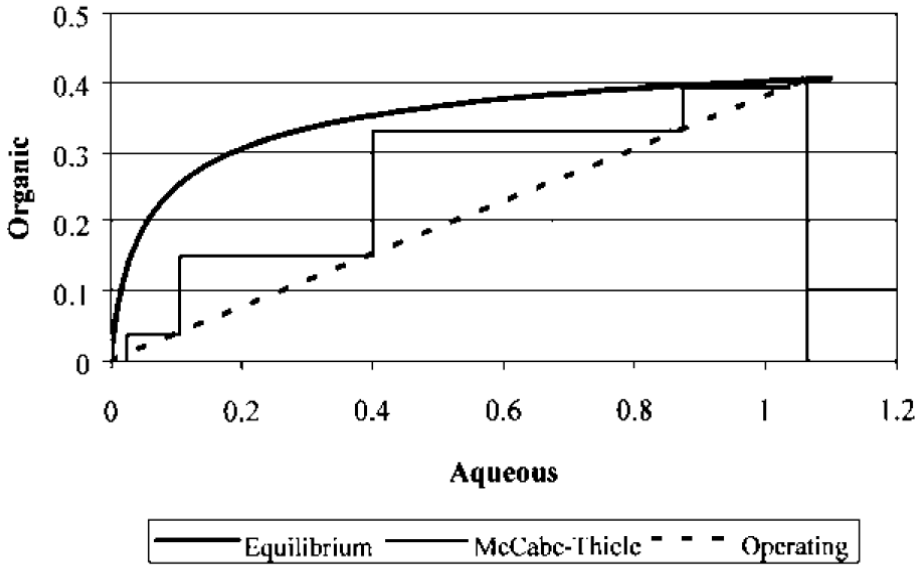

Figure 1.13:McCabe-Thiele diagram where display the decreased efficiency of SX and the number of stages (Rydberg et al., 2004)

Many extractants have been employed for experimental separation if rare earths but only few are used in industrial scale. Much information has been published regarding the extraction behavior of these extracts, the details of how the solvent extraction process works in the industry are kept confidential. SX has several advantages: 1) fast 2) continuous 3) works in more concentrated solutions 4) profitable for big quantities of material. The main disadvantage is to achieve an efficient separation of REEs, it is necessary to have more than 100 stages (including mixers, settlers, etc.) (Gupta & Krishnamurthy, 2005).

1.10 Emerging technologies for REEs extraction

There have been several attempts to use less aggressive reagents but as, yet none have shown potential as viable alternatives. The alternatives extraction processes used high temperatures (from 150 to 600 °C), pressures and high concentrations of H_2SO_4 (98%) or NaOH (70%). High energy requirements, significant associated maintenance, require corrosion resistant materials are the main disadvantages. Furthermore, highly hazardous by-products (vapours and tailings) are generated.

1.10.1 Modified processes of extracting REEs.

Chi et al., (2004) studied the chloride roasting process to extract REEs from bastnaesite concentrate. RE fluorides created from bastnaesite decomposition (under chloride roasting) are insoluble. Employing a chloride roasting process and subsequent hot water leaching may facilitate an important loss (up to one-third) of REE into the tailings. They developed a modified process to extract bastnaesite by adding magnesium oxide in the bastnaesite decomposition before chloride roasting. Thus, the fluorine reacted with magnesium oxide and created water insoluble magnesium fluoride. Therefore, recovery of REEs improved strongly (90%) with a high purity of REO produced.

Yorukoglu et al., (2003) studied the effect of addition of thiourea in H_2SO_4 in roasted and unroasted bastnaesite pre-concentrates. The pre-concentrate bastnaesite was roasted for 1 hour at 750°C to oxidize cerium and decompose. Roasted and unroasted bastnaesite pre-concentrates leached with 1-3 M H_2SO_4 and H_2SO_4 + thiourea solutions at 25°C. Roasting definitively increased REEs dissolution from 8.5% to 47.4% under the effect of H_2SO_4. Roasted pre-concentrate bastnaesite under the effect of H_2SO_4 + thiourea increased the reduction of Ce (IV) to Ce (III), thus It increased from 17.6% to 89.0% total dissolution of REEs.

Zhao et al., (2016) conducted Na_2CO_3 roasting decomposition from bastnaesite and monazite concentrate. It has two stages. The first stage consists of in air-oxidation roast where the bastnaesite decomposes. The second stage involves Na_2CO_3 roasting where more than 95% of monazite decomposes. Then, the secondary calcine is leached in H_2SO_4 and 93.7% of Th and 96.6% of REEs can be extracted.

Li et al., (2013) conducted several experiments involving leaching bastnaesite, monazite and cheralite with a HCl – $AlCl_3$ solution. Fluoride effluents are some of the most serious environmental pollutants and are found generally in fluorite and bastnaesite. RE carbonate leached easily with hydrochloric acid and rare earth fluoride is difficult to dissolve and F^- easily created complexes with Al^{3+}. With an initial concentration of 4M of HCl, the extraction of fluoride increased (after 90 minutes) from 78.86% to 97.46% when the $AlCl_3$ solution concentration climbed from 0.5M to 2M.

1.10.2 Organic acids in geochemical processes

Researchers in the area of geoscience have determined that organic acids have played an important role on a wide range of minerals, assisting dissolution of the matrix and improving elemental mobility. In Appendix A, there is a wide description of the effect of organic acids in different minerals such as basalt, feldspar, calcium carbonate – phosphate and phosphate rocks. Fulvic and humic acid (organic acids) enhance the dissolution of minerals and produce metallo-organic chelates (Huang & Keller, 1972). Organic acids and their anions (conjugate bases) improved the mineral weathering (Drever & Stilling., 1997; Wang et al., 2005). There are three factors why the organic acids influence the mineral weathering: a) changing the dissolution reaction from its equilibrium state decreasing the pH and complex formation, b) modifying how the ions are presented in solution, and c) changing compound solution saturation levels (Drever & Stilling, 1997).

In the case of carbonate-phosphate minerals, oxalic>citric>malic are the most useful acids to release P in calcareous soils in Western Iran (Taghipour & Jalali, 2013). Citric and oxalic seemed to be the most effective acids to enhance the solubilisation of phosphate rocks (Kpomblekou & Tabatabai, 1994). Geochemical processes have shown significant dissolution of REEs and might be effective in REEs' extraction. Bolan, et al (1994), Xu, et al (2004) and Goyne, et al (2010) have suggested that organic acids (particularly the low-molecular-weight organic acids - LMWOAs) exhibit suitable properties to extract REEs. The presence of LMWOAs enhanced the dissolution of rare earth elements and yttrium (REY) from monazite and apatite (phosphate minerals), indicating that mineral dissolution was raised. Citric, phthalic and oxalic acids were shown to assist the release of REY from monazite where the ligand presence in solution generally increases REY concentration. Citrate> oxalate> phthalate > salicylate are the order of ligand which promoted REY release (Goyne, et al.,2010).

Lapidus & Doyle (2015a) employed ammonium oxalate to extract uranium and thorium from monazite concentrate. The possible creation of rare earth oxalate species restrained the extraction of Th and U by passivation. The possible transformation from REEs (in monazite) to RE oxalate precipitate was achieved by 0.5M oxalate at pH 3-3.3, meanwhile, solubilisation of REEs is nil. The result of negligible solubilisation of phosphorus from the matrix. The research team kept working and attempted several methods to enhance the dissolution of Th and U by altering the oxalate re-precipitation. A solution of 0.5M oxalate and 0.5M citrate was investigated, the release of U was increased but Th only slightly. A sequential leaching with oxalate and then 1M citrate solution achieved additional recovery of 7% of Th. EDTA was used as other reagent and Th and U leached poorly compared with oxalate solutions. Only pre-treatment with concentrated (5M) caustic solution was successful in overcoming this issue (Lapidus & Doyle, 2015b).

1.10.2.1 First research to solubilise phosphates using organic acids

Johnston, H., (1952) using a "plate technique" observed that a fungal contaminant (Aspergillus niger) was able to enhance the solubilisation of dicalcium phosphate using Gerretsen's method (Gerretsen, 1948). He observed that in the periphery of the fungal settlement, there were some millimeters of clear area. Certain strains of Aspergillus niger and other members of Citromyces generate huge quantities of citric acid and smaller quantities of other organic acids when grown (Wolf & Wolf, 1947). Dicalcium and tricalcium phosphate were studied under the effect of several organic acids (gluconic, gallic, levulinic, oxalic, lactic, etc.). Five grams of calcium phosphate were grounded in a ball mill for several hours and added into 500 mL distilled water. Agar gel at 2% was prepared with distilled water and 15 mL of this added into a petri dish.

Then, 1 mL of phosphate suspension was poured into the agar (in the petri dish) while it was liquid. A N/10 solution concentration was used for the acids. The experiment ran for 6 days and most solutions diffused thorough the agar by the end of the period. The most important result of these experiments is that several organic acids were able to dissolve both compounds of calcium phosphate. The outcome of the experiments was to show that the reaction depended on the chemical structure of the acid and the pH of the solution employed.

Johnston, H., (1954a) performed more experiments with aliphatic acids and tricalcium phosphate. A sample of 1 g of tricalcium phosphate was poured in tubes where 30 mL of N/30 of each acid (maleic, oxalic, pyruvic, citric, glycolic, succinic, etc.). The tubes were placed in a reciprocal shaker and leaching tubes for 48 hours at 20°C. Oxalic acid was selected among other acids because it was thought that a precipitation effect may occur between the calcium ion and the oxalate anion and release the phosphate from the mineral. Regardless of the method used (shaking or leaching), the results are almost the same and several aliphatic acids have the ability of enhancing the dissolution of phosphates. These outcomes confirmed the former observation when using the "plate technique".

Johnston, H., (1954b) performed additional experiments with aromatic acids (phthalic, salicylic, etc.) to enhance the dissolution of tricalcium phosphate. Since most of these acids are insoluble in water, acid solutions were made N/10 in 30% ethyl alcohol. 3 g of tricalcium phosphate was added to 90 ml of N/10 of each acid. Then, they were placed in a reciprocal shaker for 48 hours at 20℃. It is noteworthy that several aromatic acids reacted with the tricalcium phosphate although they are insoluble or have low solubility in water. The results indicated that the chemical structure of aromatic acids plays an important function in the dissolution of tricalcium phosphate.

Johnston & Miller, (1959) studied the chemical reactions between organic acids and iron and aluminium phosphates to enhance the dissolution of phosphates. They concluded that the precipitation of insoluble calcium salt might be the key. For that reason, oxalic acid was included in the study due to the low solubility of calcium oxalate. They described several reactions and made some conclusions. The strength of the acid basically determines the amount of phosphate released. Furthermore, when dibasic and tribasic acid (citric) are employed, calcium created unionized association compounds and remove calcium ions from solution.

Finally, Johnston H., (1959) performed experiments with iron phosphate and aluminum phosphates under the influence of organic acids. The results indicated that several organic acids enhanced the dissolution of iron phosphates in the following order: citric>oxalic>tartaric>malic. In the case of aluminum phosphates, the organic acids were able to release phosphates into solution in the following order: citric>malic>oxalic>lactic.

1.11 Statement of the problem on REE extraction

The conventional rare earth extraction technologies, while often highly effective, have several associated issues from high cost, reagent and energy consumption to hazardous material handling and by-product generation. It is not within the bounds of conventional techniques to properly address these issues with simple process optimisation or additional infrastructure such as scrubbers. Therefore, alternative processes hold the key to cleaner, cheaper rare earth processing allowing for a more competitive international market.

Another approach is needed to process REEs on a commercial scale. Several researchers have shown, via the examination of geochemical processes, that organic acids have the ability to increase the solubility of various minerals. With respect to rare earths, it has been demonstrated that these acids have the ability to increase REE mobility and release additional anionic components from REE-bearing and similar minerals, further indicating their impact in dissolution (Kpomblekou & Tabatabai, 1994). More specifically, low-molecular-weight organic acids (LMWOAs) such as citric, oxalic and phthalic acids, intensify the mineral dissolution in apatite and monazite (Goyne et al., 2010). The studies of Lapidus & Doyle (2015a; 2015b) demonstrated that organic acids have promising properties for mineral processing of REEs. As such, literature discussing the interaction of organic acids and minerals relevant to common RE-bearing phases was examined. Based on the literature reviewed (Appendix 1), it appears that LMWOAs may present the opportunity for them to be used as an additive to, or substitute for, conventional aggressive reagents for rare earth mineral leaching.

In the present study, the main rare earth mineral of interest is monazite. Monazite is a rare earth phosphate mineral (Ce PO_4) which contains REEs from lanthanum to gadolinium (LREE). Expressed as weight percent REO, monazite usually contains between 20 – 30% Ce_2O_3, between 10 – 40% La_2O_3 and significant amounts of neodymium, praseodymium and samarium (Gupta & Krishnamurthy, 2005). Monazite has a naturally high percentage of the radioactive element Th (4-12%) and a variable content of uranium, which have a negative impact on mining and processing activities (Jha et al., 2016). Xenotime concentrate was the secondary rare earth mineral to be studied (monazite is the first) and contains most of the HREEs (from terbium to lutetium) (Zhang et al., 2016). Xenotime is a rare earth phosphate mineral (YPO_4), as is monazite, and has about 67% REO as expressed in weight percent (Gupta & Krishnamurthy, 2005).

1.12 Main Objective

The main objective of this research is to investigate and assess organic acids as alternative lixiviants to leach rare earth phosphate minerals. Currently, the common leaching agents pose potential hazards to personnel and the environment during usage; conventional processes are also quite energy intensive. Moreover, the aggressive conditions required to extract REEs from the minerals using standard lixiviants encourage researchers to find alternative agents.

1.13 Outline of each chapter

Chapter 1: General introduction, background, statement of the problem and objectives.

Chapter 2: Treatment of monazite by organic acids I: Solution conversion of rare earths

Screening experiments were conducted with monazite under the effect of several organic acids. Oxalic acid reported a significant release of phosphorus and the creation of RE-oxalate precipitated. Iron, the most important impurity, is not released in solution under 85°C. Temperature, pH and water quality play important roles in the efficiency of this stage.

Chapter 3: Treatment of monazite by organic acids II: Rare earth dissolution and recovery.

The RE oxalate precipitated was extracted into solution by EDTA. EDTA denotes a high grade of selectivity because the presence of impurities in the solution is low. The reaction is very quick (~5 mins). Temperature, water quality and pH have significant role in this stage.

Chapter 4: Rare earth hydroxide precipitation

The most common method of separation of REEs is by solvent extraction (SX) process. To feed this process, a more amenable compound is required. The creation of RE hydroxide can feed the SX without any modification of the current technology. The liquid/liquid ratio and temperature have strong effect in this stage.

Chapter 5: Comparison of the reactivity of xenotime and monazite in various systems

Monazite and Xenotime are rare earth phosphates. Although have almost the same chemical composition, xenotime reported poor results under the effect of organic acids. Mechanochemical experiments were conducted to enhance the research in xenotime but the results were not significant.

Chapter 6: Conclusions and recommendations.

Appendix 1: Research paper “Silicate, phosphate and carbonate mineral dissolution behaviour in the presence of organic acids: A review”

Appendix 2: Conference paper “Solubilisation of monazite in organic acids”

Bibliography

CHAPTER 2.
TREATMENT OF MONAZITE BY ORGANIC ACIDS I: SOLUTION CONVERSION OF RARE EARTHS

2.1 Introduction

The bulk of this chapter is constituted by the publication" Treatment of monazite by organic acids I: Solution conversion of rare earths. 2017. Lazo, D., Dyer, L., Alorro, R., Browner, R. Hydrometallurgy, (174); 202-209.

Literature is somewhat limited regarding rare earth leaching using non-standard lixiviants. Processing monazite by alkaline leaching in ball mill autoclaves has shown interesting results (Abdel-Rehim, 2002) but it is not directly applicable at the industrial scale. There have been several other studies that have attempted to use modified processes of extracting REEs with less aggressive lixiviants such as hydrochloric acid-aluminium chloride (Li et al., 2013), ammonium chloride (Chi et al., 2004) and ammonium sulphate (Moldoveanu & Papangelakis, 2013) but as yet none represent viable commercial options.

Geochemical processes have shown interesting effects on minerals relevant to rare earths that may be useful in mineral processing (Lazo et al., 2017). Organic acids have shown the ability to solubilize phosphates and the first study of this phenomenon was reported by Johnston (1952), and supported by other reports (Johnston 1954a; 1954b; 1959; Johnston & Miller 1959). Several geochemical researchers have hypothesized that organic acids, mainly the low-molecular-weight organic acids (LMWOAs), have shown promising properties that may be applied to REE processing (Bolan et al., 1994; Xu et al., 2004; Goyne et al., 2010).

Humic acids substantially aid to enhance the solubilisation of monazite. The observed improvement in the solution concentration of extracted elements and the remarkable solubilisation show these organic acids to be promising choices for hydrometallurgical processes (Polyakov et al., 2009). Rare earth ions have shown a great affinity to several organic ligands. Ethylene glycol-bis(β-aminoethyl ether)-N,N,N',N'-tetraacetic acid (EGTA), diethylenetriaminepentaacetic acid (DTPA), diaminocyclohexanetetraacetic acid (DCTA), ethylenediaminetetracetic acid (EDTA), and hydroxyethylethylenediaminetriacetic acid (HEEDTA) acids formed 1:1 complexes with rare earth ions (Topp, 1965). Moreover, the creation of compounds (trivalent rare earth ion and organic molecules) may also be useful in separation due to their properties becoming more differentiable (Speeding, 1978).

The dissolution of a variety of minerals (apatite, chalcopyrite, monazite and a range of Chinese soils) was investigated under the effect of aliphatic (citrate and oxalate) and aromatic (phthalate and salicylate) organic acids (Shan et al., 2002; Goyne et al., 2006; Goyne et al., 2010). The presence of citric, oxalic and phthalic acids was shown to aid the release of rare earth elements and yttrium (REY) from apatite and monazite (phosphate minerals), demonstrating that mineral dissolution was enhanced (Goyne et al., 2010). This discovery suggests that organic acids may be used as a substitute for, or additive to, conventional lixiviants in rare earth mineral leaching.

The binding affinity and limited solubility of oxalate ions with rare earths are employed in industrial processes as the recovery mechanism from pregnant leach solutions (PLS) (Zhang & Edwards, 2013). REEs are precipitated from conventional PLS streams using oxalate, providing a highly selective purification stage. However, other methods of using oxalate in monazite processing have been described in the literature.

Organic acids have also been tested in monazite bioleaching. Brisson et al. (2016) displayed significant improvements in leaching monazite in the presence of multiple organisms that were noted to release organic acids in the process. However, when the same acid mixtures were tested in the absence of the organisms, the leaching decreased markedly, interpreted as the acids were not the sole driver of the process. Furthermore, oxalic acid was eliminated for abiotic leaching due to the widely known insolubility of RE oxalates.

Aside from simply aiding dissolution of relevant minerals, the literature has uncovered other properties of organic acids of industrial interest, particularly that of increasing differentiation of the properties of given rare earths. This may be useful in separation (currently one of the biggest operational issues) and purification of these elements, particularly from a concentrated leach solution. The selectivity of the acids for one mineral type over another may also be of use in segregating gangue material. Overall, organic acids display significant promise in prospective use for rare earth extraction and demand further investigation.

This chapter examines the impact of organic acids on the dissolution of a monazite concentrate and describes the conversion of rare earths therein to a more amenable species. The third and fourth chapters if this thesis describes the subsequent rare earth extraction and recovery stages, respectively.

2.2 Experimental

The composition of the monazite concentrate used is given in Table 2.1. The concentrate was dried and the particle size distribution was determined (Fig. 2.1) using a Malvern Mastersizer 3000 Hydro EV. The P_{80} of 87 μm was consistent with standard industrial flotation processes allowing the results to be easily related to current practices. Some elements were assayed in the majority of the tests.

Table 2.1: Relevant elemental composition of the monazite concentrate

Element	Grade (wt %)	Element	Grade (wt %)
La	8.65	Pr	1.75
Ce	14.36	Sm	0.76
Nd	3.32	Gd	0.27
P	7.24	Y	0.12
Fe	16.25	Th	0.0012

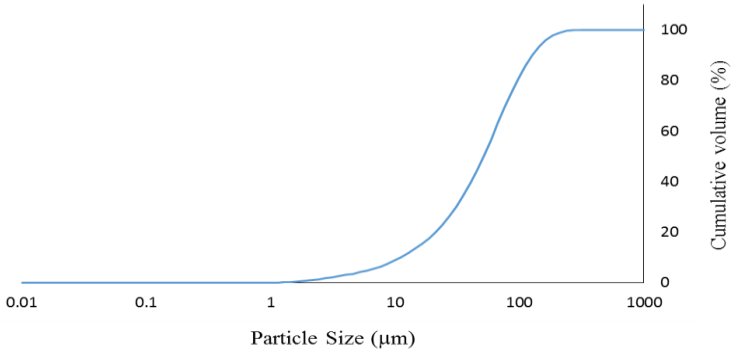

Figure 2.1: Particle size distribution of the monazite concentrate.

Powder X-Ray diffraction analysis (XRD) was conducted using an Olympus BTX-II diffractometer to gather structural information. Solutions were analyzed by an ICP-OES (Agilent 5100 Synchronous Vertical View-SVDV). Oxalic, tartaric, acetic, formic, mandelic, levulinic, gluconic and citric acids were all analytical grade reagents. Crotonic, maleic, lactic and sulphuric acids as well as sodium hydroxide were laboratory grade.

Screening experiments were conducted to determine the impact of each organic acid on both the monazite and major gangue phase. The experiments were performed in stoppered, 250 mL Erlenmeyer flasks. The type of organic acid and pH (2 and 5) were the primary variables tested with molar concentration, temperature, solid/liquid ratio and leach time all being constant.

Monazite concentrate (10 g) was added to 100 mL of solution of each organic acid, which had been set to the appropriate pH using sodium hydroxide or sulphuric acid. Once thoroughly combined, the flasks were placed in a Labwit ZWY-211B incubator shaker at 100 rpm and 25 °C for 24 hours. The solutions were filtered and a sample of solution taken for analysis before the solids were washed with deionized water.

Oxalic acid, the most promising reagent, was then selected for further investigation. Larger scale tests were conducted in either a 1 L Duran flat range reaction vessel or 2.2 L custom stainless steel reactor, agitated using a Heidolph Model RZR-1 overhead stirrer. The impact of additional variables (acid concentration, temperature and solid/liquid ratio) were investigated with 10 mL solution samples taken over time to examine the influence of reaction time. All solution samples were analyzed by ICP-OES for elemental composition and selected solids were characterized by XRD to determine the phases in the leach residue.

Rare earth oxalate was synthesized from solution generated by water leaching after acid roasting the concentrate, for comparison to the samples obtained by the organic acid route. Monazite (100 g) was added to 85 mL of sulphuric acid (98 %). Once thoroughly combined, the mixture was placed in a Furnace Industries PF-62B2C-M furnace for 4 hours at 210 °C and the mixture was left to cool for 12 hours. Then, 450 mL of water was added to the mixture to solubilise the rare earth sulphate with stirring at 500 rpm for 4 hours. The slurry was filtered and the solids were washed with deionized water. The generated solution was diluted with 2.5 L with deionized water. The pH of the diluted solution was increased to 1.5 by adding ammonium hydroxide (30 %). Finally, 125 mL of oxalic acid (2.1 M) was added to the rare earth sulphate solution and placed in a glass reactor at 500 rpm for 2 hours at ambient temperature (~25 °C) (Barghusen & Smutz, 1958; Welt & Smutz, 1958). The solution was

filtered and the solids were washed with deionized water. The solution was analyzed by ICP-OES and the solids were characterized by XRD.

An electrochemical process defined by Turhan et al. (2011), was used to examine the concentration of oxalate ions. Differential pulse voltammetry (DPV) was conducted across standards between 1 and 20 mM oxalic acid along with samples sufficiently diluted to fall within the calibration range. A background electrolyte of 0.2 M sodium sulphate was used for the standard solutions. The voltametric scan was conducted from 0 to 2 V at a rate of 50 mV/s.

Additional experiments were performed using tailings water from the same mine site where the concentrate comes from, the major impurity components are described in Table 2.2. Mine sites have vast volumes of tailings water available where natural water sources are limited, particularly those meeting purity requirements for processes. Additionally, most of the mines site are located in remotes locations which made water transport uneconomical. Therefore, recycling tailings water has several important aims: reduce the volume of tailings water, reduce the volume of purified water to be used, reduce the cost of operation and maintenance of the tailings ponds. Deionized and tailings water were both used for the 72 h experiment to determine the impact of water quality. In each experiment, the slurry was filtered and the solids were washed with deionized water.

Table 2.2: Analysis of tailings water.

Element	Units	Quantity
pH in water	pH units	7.9
Total dissolved solids (grav)	mg/L	3100
Total suspended solids	mg/L	20
Sodium dissolved	mg/L	1100
Bicarbonate HCO_3 as $CaCO_3$	mg/L	320
Chloride in water	mg/L	1100
Sulphate in water	mg/L	690
Hardness as $CaCO_3$	mg/L	290
Silica dissolved	mg/L	120

2.3 Results and discussion

2.3.1 Screening tests

Initial screening tests were conducted to determine the impact of various acids at pH 2 and 5 (Fig. 2.2 and 2.3, respectively). Values from acetic, formic, levulinic, crotonic and lactic acids are not presented due to negligible dissolution of any measured element. Cerium and lanthanum concentrations in the leaching solution were studied as the most prolific rare earths in the concentrate. Nd, one of the most valuable LREEs, was studied in the last experiment. Phosphorus concentrations provided another point of measure for the decomposition of monazite where REE concentrations were not indicative. Iron oxides represent one of the most abundant impurities in the concentrate (most likely present predominantly as goethite),

therefore the concentration of iron was measured to determine if organic acids enhance its dissolution.

A varied response in the release of elements from monazite was observed in the presence of different acids. Oxalic, maleic and tartaric acids induced the greatest degree of phosphorus dissolution in acidic conditions indicating the greatest impact on REE-bearing minerals. The relative impact of the acids relates well to literature values for the binding strength of organic acids with the elements. Oxalic acid at pH 2 displayed the greatest impact on iron and phosphorus, but with relatively low rare earth dissolution. Citric acid released a greater proportion of the rare earths with much lower phosphorus concentrations. This suggests conversion of the monazite rather than direct dissolution in some cases, supported by the observations of Lapidus & Doyle (2015a).

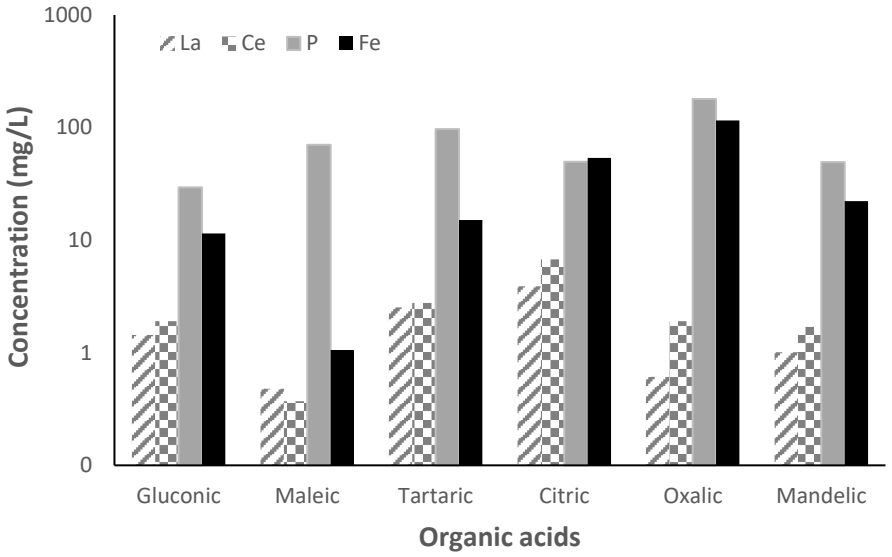

Figure 2.2: Leaching monazite for 24 hours in 0.2 M acids at pH 2 and 25°C

The response at pH 5 was markedly poorer, with lower proportions of all elements being present in solution for every system except for citric acid. Interestingly, citric acid released greater amounts of rare earths, but even less phosphorus than in the pH 2 tests. None of the tests however, resulted in significant dissolution. The trend is likely related partially to the binding strength of the ligand to the mineral surface. Higher pH levels will create a more negative surface, thus decreasing the electrostatic attractive force between the surface and the negatively charged ligand. Similarly, the degree of protonation of the organic molecules will impact the strength of the complex formed with the relevant elements. Other impacts may be due to the effect of acid attack as a dissolution mechanism and pH on the solubility of the constituents.

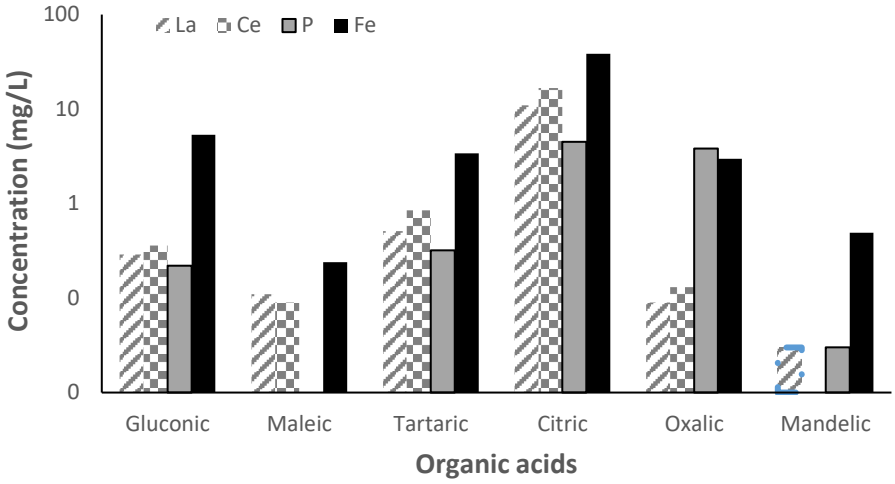

Figure 2.3: Leaching of monazite for 24 hours in 0.2 M acids at pH 5 and 25°C

Oxalic acid system: As oxalic acid exhibited the greatest influence on the dissolution of phosphate minerals at a pH of 2 and has shown promising behavior in previous research, it was investigated further. While citric acid dissolved the greatest proportion of REEs from the concentrate, these were still very low levels with no indication that greater dissolution could be achieved with more aggressive conditions. Therefore, conversion of the REEs with oxalic acid was the targeted approach.

2.3.2 Thermodynamic aspects

Medusa software (Puigdomenech, 2013), was employed to create the thermodynamic diagrams presented in this study (Fig. 2.4). The data references for the Medusa software (Hydra database) was used without any addition of data, producing very similar results (Ce and Nd) to those reported by Lapidus & Doyle (2015a). Several researchers reported that thermodynamic data may differ due to variations in the crystal structure and degree of hydration of the phases present (Liu & Byrne, 1997; Cetiner et al., 2005). It should be noted that the software performs the calculation of all possible equilibrium reactions of the species, therefore, those reactions that are kinetically unfavourable should be discarded. The diagrams presented in figure 2.4a-c were calculated based on the proportions of elements present in the system under standard 100 g/L solid concentration.

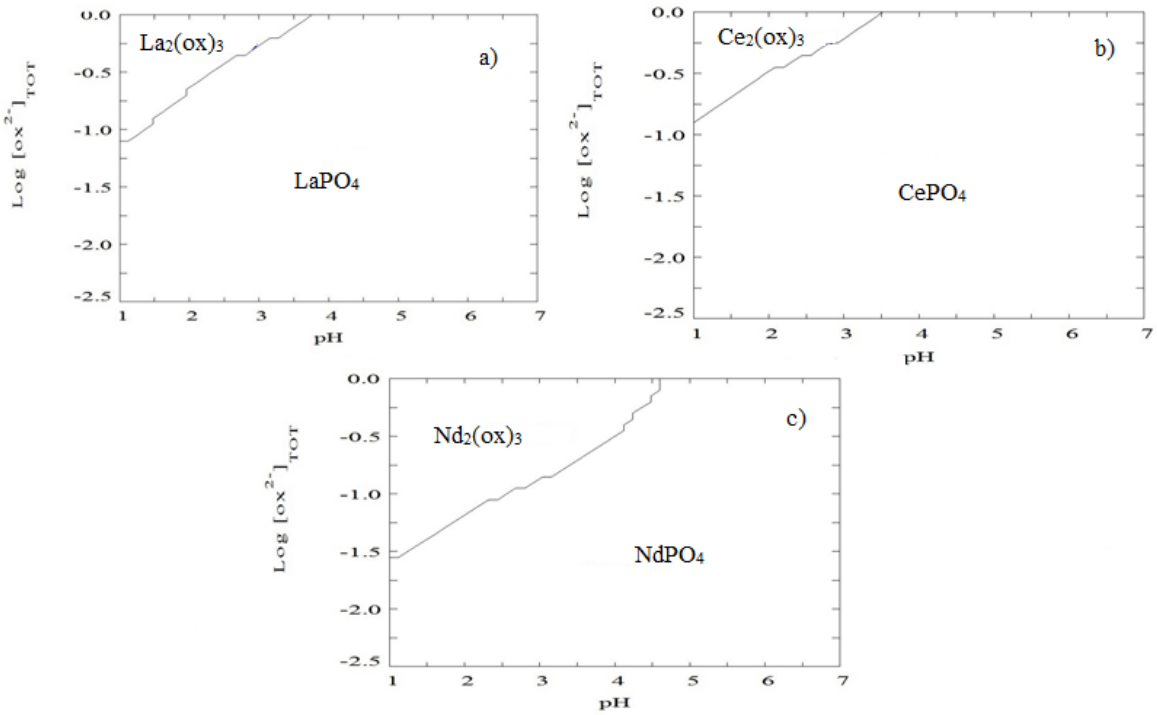

Figure 2.4: Stability diagrams for a) lanthanum, b) cerium and c) neodymium as function of oxalate concentration and pH. Conditions: 25°C, 0.233 M PO_4^{3-}, 0.0062 M La^{3+}, 0.102 M Ce^{3+} and 0.023 M Nd^{3+} respectively.

Figure 2.4 shows that at low pH and significant oxalate concentration, the rare earth oxalates are thermodynamically preferred over their respective phosphate species. Ce and La are the most prolific REEs in the monazite concentrate but the least valuable per unit mass. These elements have similar stability regions suggesting similar behaviour may be observed in these systems. Figure 4c suggests Nd oxalate is more favoured than the respective La and Ce species, being formed at lower oxalate concentrations and across a wider pH range. This may suggest that during conversion, the $NdPO_4$ component may react preferentially to the other REEs.

2.3.3 Conversion Leaching

Monazite concentrate (100 g) was added to 1 L oxalic acid (1 M, pH 1) in a 1 L Duran reactor vessel and agitated at 500 rpm for 24 hours and 25°C. The larger scale of the experiments also allowed for reliable data to be collected over time. It is noted that oxalic acid solubility was a significant issue at 1 M oxalic acid, particularly during pH adjustment. A fifty-fold increase in the proportion of phosphate that dissolved was observed (Fig. 2.5) with respect to the screening tests. Whether this is the influence of the increased acid concentration, decreased pH or more vigorous agitation (or a combination thereof) is unclear. As in previous testing, the rare earth concentration did not exhibit a similar increase. This confirms that the rare earth deportment in the system is significantly different to the phosphorus, most likely a solution conversion to another species.

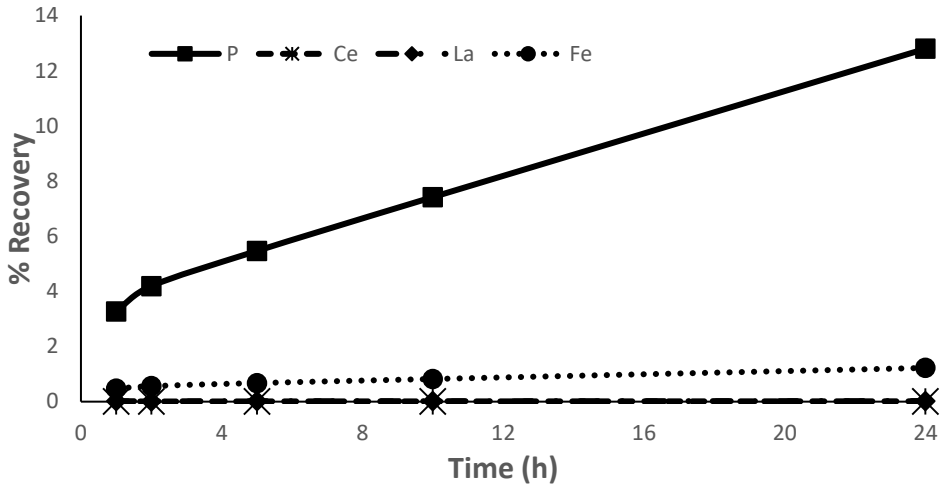

Figure 2.5: Leaching of monazite for 24 hours at pH 1, 500 rpm, 1 M oxalic acid and 25°C

Further tests were conducted to determine the impact of oxalic acid concentration and solid/liquid (S/L) ratio over longer time periods. Agitation rate, temperature and pH were fixed across these tests. Achieving pH 1 at high oxalic acid concentrations (> 0.8 M) was very difficult due to saturation of the acid, therefore a pH 0.7 was selected. The experiments containing 100 g/L of monazite show a good correlation between phosphorus release and oxalate concentration (Fig. 2.6). The 1 M and 0.8 M systems produced similar results, suggesting a limitation in reaction rate exists at high concentrations. Comparing the 0.2 M experiment with the screening test results, it appears that the lower pH has a significant impact on mineral dissolution as more than three times as much phosphorus was released in this experiment as the screening test at the same oxalic acid concentration. While the more thorough mixing of the agitated vessel would likely have aided this, it is unlikely to have increased the dissolution by such a magnitude. On a similar note, the difference between pH 1 and pH 0.7 seems to have made little impact with phosphorus release in the 1 M system being comparable to that achieved in Figure 2.5.

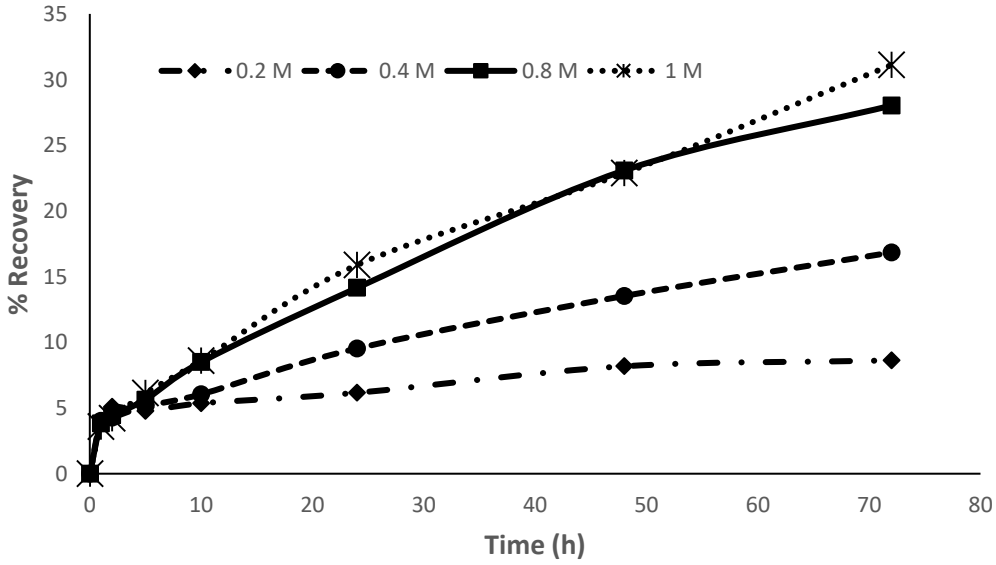

Figure 2.6: Recovery of phosphorus from monazite over 72 hours at pH 0.7, 500 rpm agitation, S/L: 0.1, and 25°C

Upon doubling the solid/liquid ratio the solubility constraints on the 1 M system become more apparent (Fig. 2.7). While, the 1 M system releases somewhat more phosphorus than the 0.2 and 0.4 M leach solutions, 0.8 M acid achieves by far the greatest recovery. However, the overall recovery has not only dropped with the higher solids content, the solution concentrations reached were actually lower. This led to a recovery of less than half that of the 100 g/L tests concentrate for all systems except 0.2 M. This implies that the system is not overly flexible in regard to solids concentration of process slurries and the ideal S/L ratio is definitely below 0.2 and potentially 0.1. However, this may be managed using approaches such as continuous reagent addition across multiple reactors.

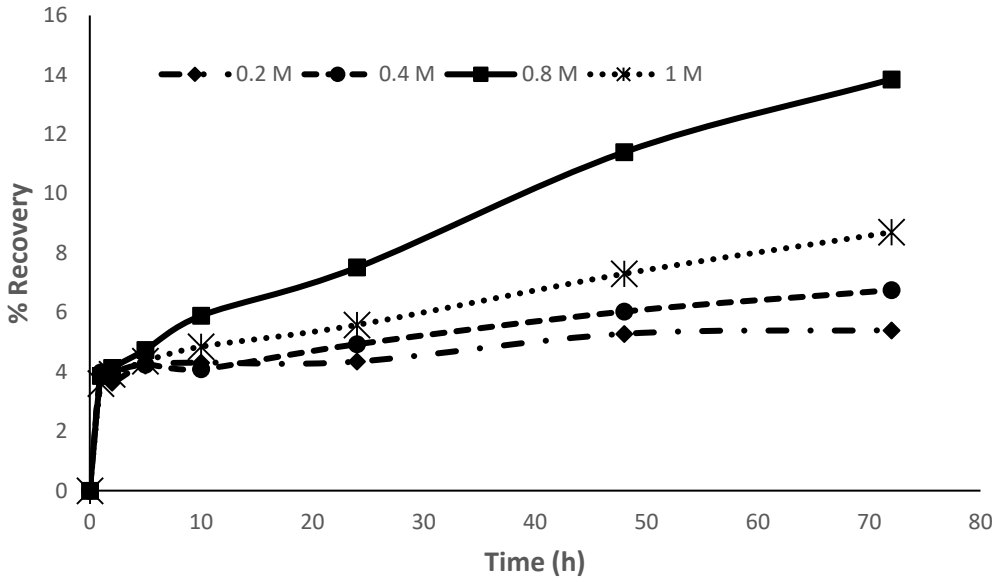

Figure 2.7: Recovery of phosphorus from monazite over 72 hours at pH 0.7, 500 rpm agitation, S/L: 0.2 oxalic acid and 25°C

The final recoveries after 72 hours of all of the S/L systems (150 g/L system was tested but is not individually displayed herein) are presented in Figure 2.8. Based on the relative ability to deal with varied solids contents and the ease of preparation (no solubility issues), 0.8 M acid was considered an optimal value for further testing.

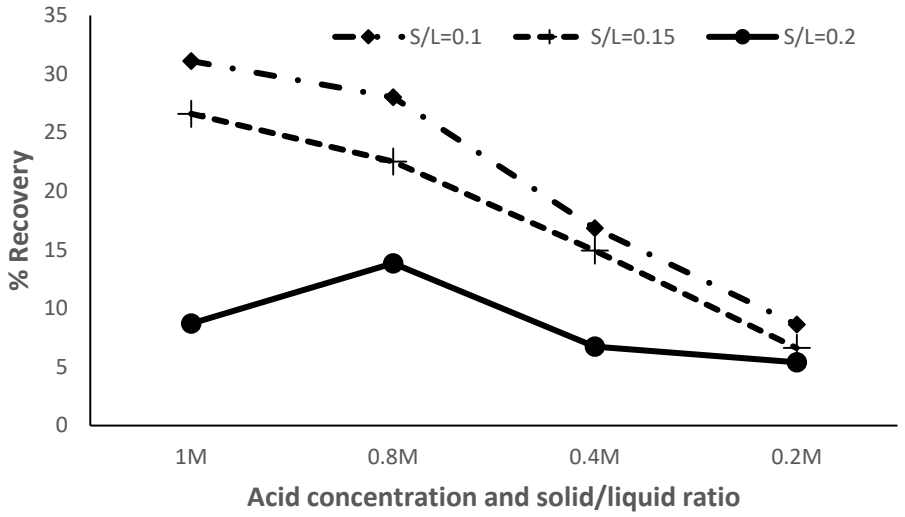

Figure 2.8: Recovery of phosphorus after 72 hours at pH 0.7, 25°C and 500 rpm agitation with varied oxalic acid concentrations and S/L ratios

A 10 hours experiment was conducted at a temperature of 65°C, pH 1, 0.8 M oxalic acid and a S/L ratio of 0.1 (Fig. 2.9). The elevated temperature greatly accelerated the rate of phosphorus release, achieving comparable levels to 72 hours time at ambient temperature. Meanwhile, the proportion of rare earths present in the leachate is still insignificant. The other point of note is that iron dissolution increased by more than an order of magnitude.

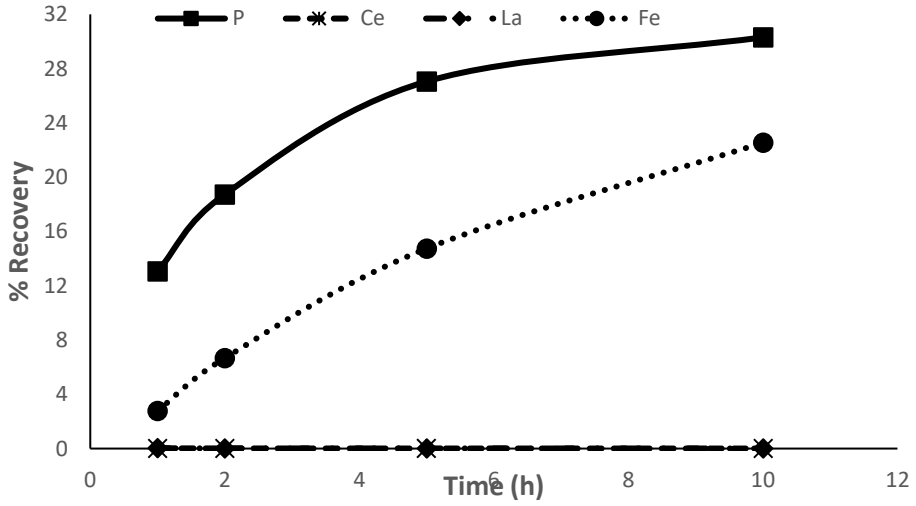

Figure 2.9: Elemental recovery during leaching with 0.8 M oxalic acid at 65°C, pH 1, 500 rpm agitation and a S/L ratio of 0.1

Although not observable in Figure 2.9, the concentrations of both La and Ce peaked in the 1 hour sample and decreased over time. This is consistent with re-precipitation as an insoluble species. The concentrations only reached approximately 2 and 2.8 ppm respectively, which is comparable to that reached at ambient temperature, suggesting temperature has little impact on the re-precipitation or solubility of the rare earth species formed. From Figure 2.9 (50g/500mL) 1 hour leaching: P, 945 mg/L; Ce, 2.8 mg/mL; La, 2 mg/mL; Fe, 452 mg/mL; Nd, 1 mg/mL and Pr 0.4 mg/mL.

Another 10 hours experiment was conducted at 85 °C, pH 1, 0.8 M oxalic acid and a S/L ratio of 0.1 (Fig. 2.10). The elevated temperature greatly accelerated the rate of iron dissolution and while the initial phosphorus release was accelerated the maximum achieved was lower. The increase in iron dissolution has significant potential implications for downstream processing and by-product recovery. As phosphate may potentially be recovered, the much greater proportion of iron impurity may impede such a process or contaminate the product. Conversely, with regard to the rare earths, their recovery from the residue may be more efficient if more of the iron-based gangue has been removed. This may be achieved either through lower impurity levels in the extraction process or less occlusion by insoluble iron minerals.

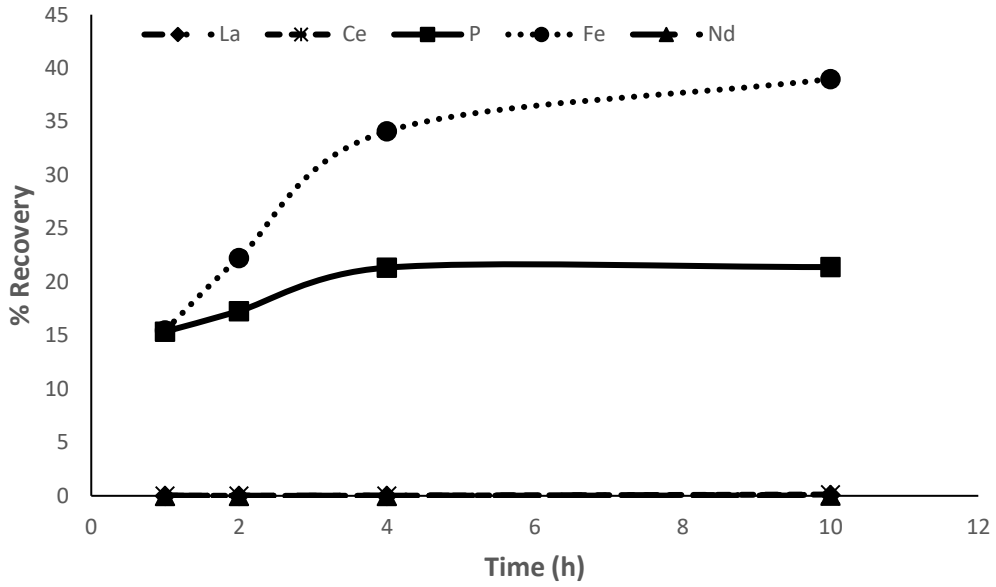

Figure 2.10: Elemental recovery during leaching with 0.8 M oxalic acid at 85°C, pH 1, 500 rpm agitation and S/L ratio of 0.1

The residue from the previous experiment was leached with a fresh oxalic acid solution with the same conditions at elevated temperature (85°C) (Fig. 2.11). The same pattern of the previous experiment can be observed where iron release was high to the detriment of phosphorus release and rare earth elements dissolution was still insignificant. It seems that due to oxalic consumption, the reaction stopped.

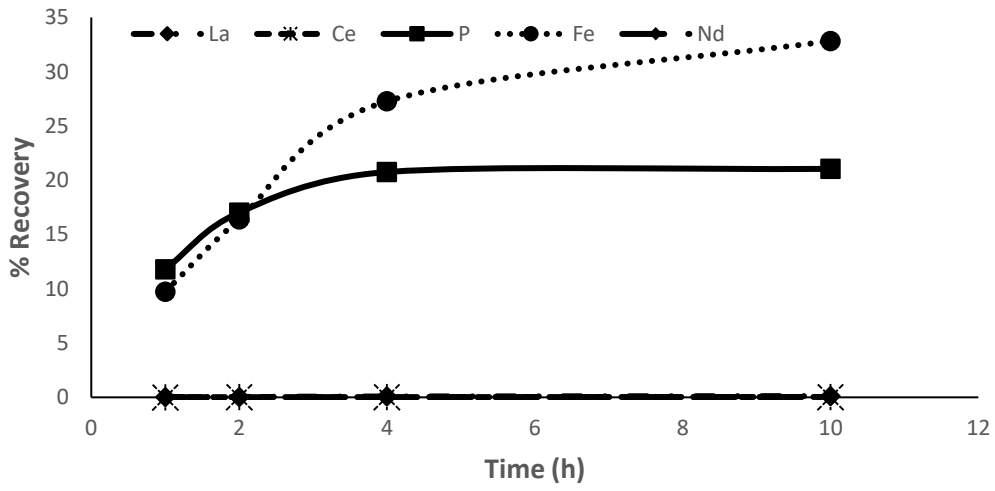

Figure 2.11: Elemental recovery during leaching with 0.8 M fresh oxalic at 85°C, pH 1, 500 rpm agitation and S/L ratio of 0.1

As the rate of phosphorus release (and thus conversion) decreases over time, stopping well short of entirety, tests were conducted to determine the limiting factor and identify potential methods to increase recovery. Based on the work of Lapidus & Doyle (2015a, b), it is suggested that passivation of unreacted material by the re-precipitating rare earth oxalate may inhibit further conversion. The monazite was pulverised resulting in an overall P_{80} of 45 μm and then leached under similar conditions. The lack of improvement in the extent of reaction when leaching this material is an indicator that passivation may not be the primary limiting factor.

The variation between the results obtained in the screening tests and those at larger scale indicate that increased acidity and oxalate concentration are vital for the conversion reaction. The solution pH of tests at various temperatures was measured after 10 h of leaching to determine whether significant acid consumption contributed to the deceleration/cessation of the reaction (Table 2.3). The solution samples were cooled to ambient temperature before measurement so that the pH could be directly compared. As can be seen there was not a significant increase in the pH in any of the tests showing that acid consumption is unlikely to be a contributing factor. It is evident from the dependence for the reaction on pH and free oxalate concentration that the mechanism of dissolution is a combination of proton attack and complexation leaching.

Table 2.3: Solution pH obtained from tests conducted at various temperatures after 10 h (initial pH = 1, 0.8 M oxalic acid, 100 g/L concentrate).

Reaction temperature	pH
25 °C	1.24
45 °C	1.03
65 °C	1.06
85 °C	1.03

Figures 2.6 and 2.7 display the importance of oxalic acid, the influence of the reagent's consumption was tested via multiple methods. Two room temperature oxalic acid leach tests were run for 168 h, at which time the rate of phosphorus release had declined significantly. 200 mL of fresh leach solution was then added to one of the reactors (Fig. 2.12), while the other system was filtered and the residue was placed in 1 L of fresh leach solution (Fig. 2.13a & b). The data in Figure 2.12 was adjusted for dilution.

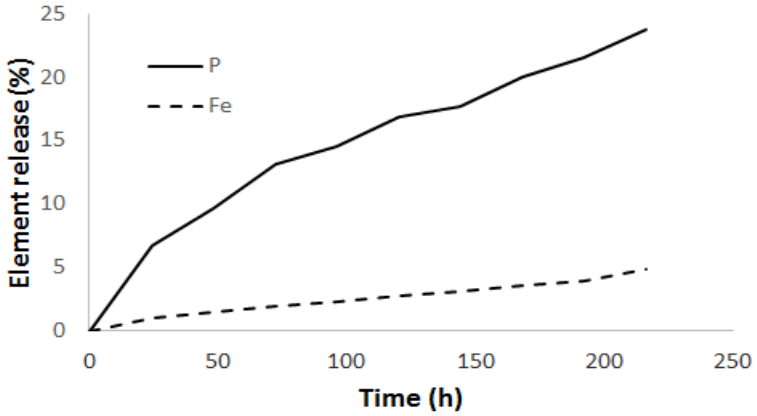

Figure 2.12: Fe and P release from a leach (25°C, 0.8 M oxalic acid, 100 g/L concentrate), 200 mL of fresh solution added after 168 h (values adjusted for dilution).

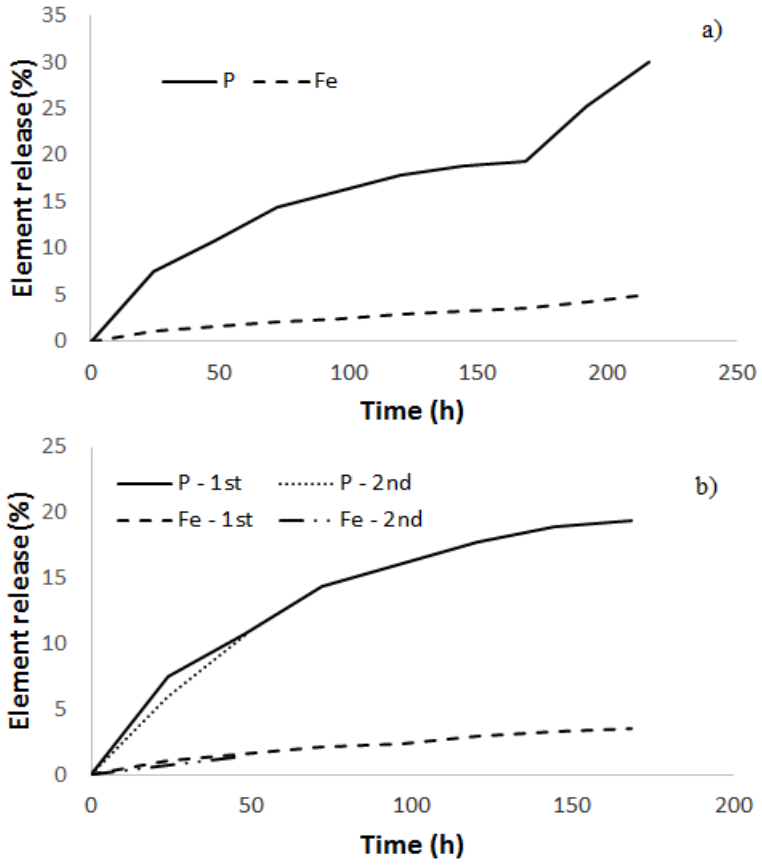

Figure 2.13: Fe and P release from a leach (25°C, 0.8 M oxalic acid, 100 g/L concentrate), residue filtered after 168 h placed in fresh solution, where a) further reaction is shown as additional time and b) reaction in fresh solution is compared to initial.

Both systems showed continued P release when the solutions were altered. The additional acid applied to the system allowed for an apparent slight increase in phosphorus release, suggesting there is at least some dependence on oxalate concentration. The fresh solution applied to the residue greatly accelerated phosphorus release after it had declined over time in the first leach stage. Comparison of the proportion of P leaching between immersion in the initial and second solutions showed roughly equivalent levels, suggesting there is little or no inhibition of the reaction from passive layers of reaction products. Given the data in Table 2.4 and Figures 2.12, 2.13a & b, it is apparent that free oxalate concentration is the primary limiting factor in the extent of reaction as opposed to acid consumption or passivation. This seems to be an important factor in temperature selection as greater iron leaching will decrease the free oxalate concentration significantly. Temperature played an important role in iron dissolution and free oxalate consumption. Decreasing the temperature was an important countermeasure to minimise iron dissolution.

The effective oxalate concentration was investigated to confirm this assertion. The use of differential pulse voltammetry is indicative of concentration rather than giving a definitive value. The values would also most likely be related more closely to oxalate activity in leach solutions given the chemical's affinity for complexation (effectively a measure of free oxalate). Samples of leach solution after 10 h of leaching at 25, 45, 65 and 85 °C were tested. Based on the peak intensity of the calibration standards, the concentration in all samples was equivalent to less than a 0.1 M oxalate solution. Given the drastically decreased leaching observed in the 0.2 M system, this would lead to significantly reduced leaching. Increasing temperature raised the dissolution of iron (and thus oxalate consumption) and decreased the dissolution of phosphorus. The presence of high quantities of iron may have an important effect for downstream processing and need further investigation.

2.3.4 Analysis of Conversion Product

The oxalic acid leach residue was analysed by XRD and compared with the original concentrate (Fig. 2.14), which showed that another phase was being formed during the leach process. This phase could not be identified using the database available as the database did not contain any rare earth oxalate species. Therefore, in an attempt to identify the new phase, rare earth oxalate crystals were formed using standard industry practice as outlined in Barghusen and Smutz (1958) and Welt and Smutz (1958). Analysis of this material confirmed that the phase formed in leaching was in fact a rare earth oxalate. Equation 2.1 describes the potential reaction.

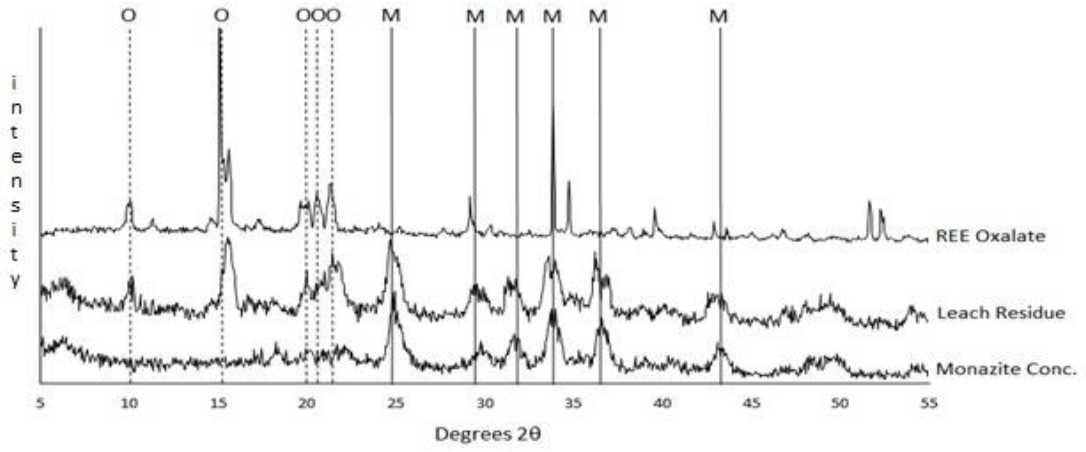

Figure 2.14: XRD patterns obtained from monazite concentrate, oxalic acid leach residue (0.8 M oxalic at 65°C, pH 1, 500 rpm agitation and S/L ratio of 0.1) and synthetic rare earth oxalate samples.

$$2REPO_{4\,(s)} + 3H_2C_2O_{4\,(aq)} \rightarrow RE_2(C_2O_4)_{3(s)} + 2H_3PO_{4(aq)} \quad (2.1)$$

$$Fe_2O_3 + 3H_2C_2O_{4\,(aq)} \rightarrow Fe_2(C_2O_4)_3 + 3H_2O \quad (2.2)$$

2.3.5 Tailings water

Recycling tailings water can be very economical in the performance of the operation of the mine not only of the amount of water use in the process but also in the volume of tailings discarded. Water supply is scarce and expensive in remote areas where most of the mines operated. Several metallurgical processes (i.e. flotation) discard great quantity of tailings water, it can be economically beneficial to use reclaimed tailings water in processing.

The target pH (1) was not able to be reached as precipitation occurred in raising the pH, therefore a lower pH (0.7) was set. One possible driver of low solubility is the existence of significant suspended and dissolved solids in the tailings water. The impurities in tailings water have a remarkable influence on the reaction extent resulting in significant reduction in solution concentration of phosphorus (approximately 41 % decrease) (Figure 2.15). The water contains elevated levels of several elements including calcium. The significant concentration of calcium may lead to the creation of an insoluble calcium oxalate coating on the particle surface (Gierlus et al., 2012). This and the presence of other free ions in water may also impede or decrease the availability of oxalate in solution.

The decrease in phosphate release observed in Fig 2.15 shows that direct use of tailings water is not suitable for this stage. The impact of the presence of suspended and dissolved solids has too great an influence on the conversion to RE oxalate. However, if the mechanism for this inhibition is understood economic treatment of the water may deem it usable in this system. Due to the scarcity of pure water and the cost of its generation, this is a key issue in the development of a viable process.

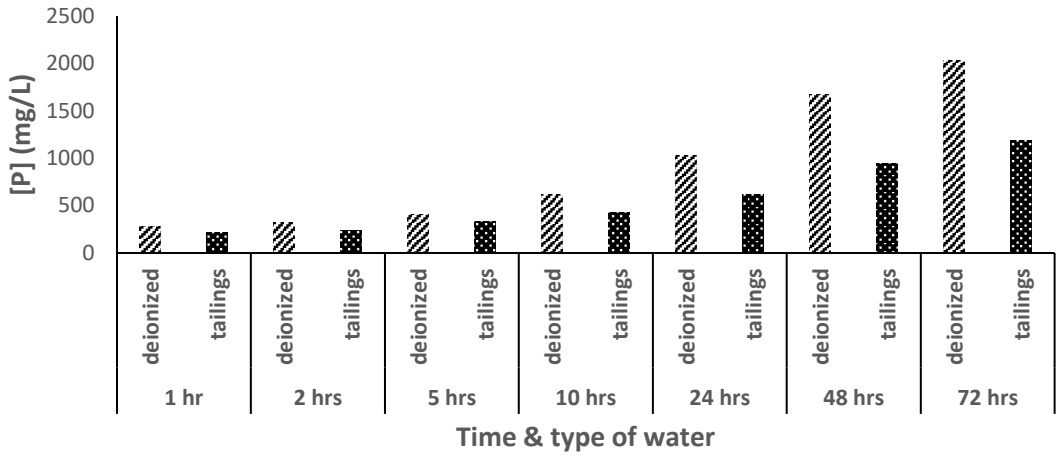

Figure 2.15: Comparison leaching of phosphorus in monazite 0.8 M oxalic acid S/L: 0.1 for 72 hours at pH 0.7 using ionized and tailings water and 25°C.

In Appendix 2, there is more information related to this section.

2.4 Conclusions

Oxalic acid has proven to greatly promote the dissolution of monazite, marked by the release of phosphorus into solution, even at ambient temperature. The fact that the rare earths were not observed in solution to a similar magnitude was proven to be due to the formation of a solid rare earth oxalate. Iron was not released in a great proportion at ambient temperature in direct contrast to its known affinity for the formation of iron oxalate complexes. Oxalic acid (0.8 M) at pH ≤ 1.3 was seen to be the optimal leach solution based on recovery of phosphorus and solubility limitations. Recoveries drop significantly at elevated solids concentrations, again indicating that solubility issues are significant. Elevated temperature (65°C) accelerated the phosphorus release, achieving a similar reaction extent after 10 hours as obtained after 72 hours at ambient temperature. At 85°C, the iron released was vastly increased to the detriment of phosphorus. This also vastly increased iron dissolution having implications for downstream processing and by-product formation. Limitation of the reaction extent was found to be caused by oxalate consumption, while passivation appeared not to have a significant influence. Tailings water used to test the impact of dissolved and suspended solids on the process showed a marked decrease in phosphorus release, suggesting a significant decrease in monazite conversion to RE oxalate. Water purity will thus be a significant issue moving forward with this technology.

CHAPTER 3.
TREATMENT OF MONAZITE BY ORGANIC ACIDS II: RARE EARTH DISSOLUTION AND RECOVERY

3.1 Introduction

The bulk of this chapter is constituted by the publication" Treatment of monazite by organic acids II: Rare earth dissolution and recovery. 2017. Lazo, D., Dyer, L., Alorro, R., Browner, R. Hydrometallurgy, (179); 94-99.

EDTA is known to form complexes with almost all metal ions with a positive charge greater than one (West, 1969). Therefore, there is concern over the selectivity of the REE extraction. Chang & Matijevic (1983) displayed the ability of EDTA (0.1M) to enhance the dissolution of iron from hematite in alkaline conditions (pH ~10) at 25°C. Misumi & Taketatsu (1959) showed that an REE oxalate salt can be dissolved in the presence of an excess of EDTA with a rapid reaction rate at 60°C (Misumi & Taketatsu, 1959). Furthermore, the dissolution of hydroxyapatite immersed in EDTA had a significant dissolution period between 1 and 3 mins (Arbel et al., 1991). The solubility of the RE oxalate in EDTA was studied by Bhat & Venkateswara (1964) where the solubilities depended on the stability constants of the EDTA complex. In that study the pH of the equilibrium was raised, increasing the solubility.

In Chapter 2, the formation of a RE oxalate precipitate was empirically demonstrated. The apparent reaction for the pre-treated monazite concentrate under the effect of oxalic acid is given by Equation 2.1. The products thereof would be used to create the tentative chemical reaction in the sequential leaching described later.

To sum up, several organic acids have strong affinity to chelate metal ions. The degree of complexation depends on the values of the parameters, the type of chemical structure and the process undertaken. On industrial scales, it is common to use low concentrations and inexpensive reagents, so the profitability of the project may be assured.

3.2 Experimental

3.2.1 Materials

The primary components of the monazite concentrate was determined by XRF, structural information analysis was performed by Powder X-Ray diffraction analysis (XRD) employing an Olympus BTX-II diffractometer and particle size distribution by Malvern Mastersizer 3000 Hydro EV with all data reported in Lazo et al. (2017). The average composition of the residue from the oxalic acid conversion stage, obtained through aqua regia digest and ICP-OES, is provided in Table 3.1. Some elements were assayed in the majority of the tests.

Table 3.1: Relevant elemental composition of the residue from the oxalic conversion leach

Element	Grade (wt %)
La	7.5
Ce	12.7
Nd	5.3
P	4.1
Fe	12.5

The pre-treated monazite concentrate was studied under the effect of the following organic acids: formic (AR), acetic (AR), levulinic (AR), gluconic (AR), tartaric (AR), citric (AR), mandelic (AR), EDTA (AR), lactic (LR), crotonic (LR) and maleic (LR). Sodium hydroxide (AR) was acquired from Chem-Supply and sulphuric acid (AR) from Thermofisher.

Oxalic acid pre-treatment, described in the first paper in this series (Lazo et al., 2017), of the monazite concentrate for the majority of these experiments was conducted under the following conditions: 0.8 M oxalic acid, pH 1, S/L: 0.1, 500 rpm, 25°C and 72 hours reaction time. The exception being experiments at elevated temperature (45, 65 & 85 °C), where the residence time was reduced to 10 hours. The proportion of phosphorus leached during this initial stage is indicative of the proportion of monazite conversion; it is important to the limitations on secondary leaching and is thus added to the figure captions for comparison (given as % P removal).

3.2.2 Methods

Screening experiments were carried out to determine the most effective organic acids for extracting rare earth elements from the pre-treated monazite concentrate. The experiments were performed in stoppered 125 mL Erlenmeyer flasks. The acid species, concentration and solution pH were the first conditions tested while residence time, solid/liquid ratio and temperature were kept constant.

Pre-treated monazite concentrate (5 g) was combined with 50 mL of 0.1 M solutions of each organic acid at the required pH. Once thoroughly combined, the flasks were placed in a Chiltern Scientific orbital shaker and agitated at ambient temperature for 24 hours. The solutions were filtered and the solids were washed with deionized water. The solutions were analyzed by ICP-OES (Agilent 5100 Synchronous Vertical View SVDV).

EDTA, the species which achieved the greatest extraction, and citric acid (previously described in REE chelation studies), were chosen for further study. Larger scale experiments were carried out in a 1 L Duran glass reaction vessel agitated by a Heidolph Model RZR-1 overhead stirrer with 100 g of pre-treated monazite concentrate at 25°C for 72 hours. Residence time, acid concentration, solution pH and stirring speed were all tested with 10 mL solution samples taken incrementally over time to examine leach performance. Optimal conditions were then further tested to determine the efficiency of the oxalate conversion leach.

Further experiments with EDTA were conducted employing tailings water (under the same set up conditions at 25°C from the mine site) and the composition of the tailings water can be observed in Table 2.2. In the experiment, the slurry was filtered and the solids were washed with deionized water. Water supply is an important commodity in regional areas where most of the mine site are located. The utilization of tailings water can increase the economical approach of a mine operation where water is crucial ingredient.

3.3. Results and discussion

3.3.1 Screening experiments

The solution concentrations of cerium, lanthanum, and neodymium were selected for analysis as they represent the most prolific REEs in the sample. Phosphorus and iron solution concentrations were measured for comparison as they are the predominant impurity elements in the sample to determine if selective leaching of the REEs occurred.

Varied results in the extraction of elements from the pre-treated monazite concentrate were found when immersed in different acids. Alkaline EDTA reported the highest extraction of REEs from the pre-treated monazite concentrate. Citrate, tartrate and lactate produced very similar results. In addition to EDTA, citrate has been chosen as another possible leaching

reagent for several reasons. It was the first efficient eluent in the ion-exchange separation process of REEs (Warren et al., 1947; Spedding et al., 1947) providing comparison data, it is a comparatively inexpensive reagent, and citrate has the second highest stability constants for REE complexes (EDTA>citrate>tartrate>lactate) (Martel & Smith, 1977). Iron dissolution was not substantial, which is logical as a significant amount of the soluble iron was removed during pre-treatment of the monazite concentrate with oxalic acid and the stability constants of iron complexes of these four compounds are relatively low compared to those of REEs.

3.3.2 Large Scale Testing

EDTA was the most promising organic acid and as mentioned citrate had performed well in other applications, thus experiments on a larger scale were carried out to compare and optimize their performance. Upon more rigorous testing, both acids achieved significant extraction of the REEs and released low concentrations of the impurities (P and Fe) as shown in Figures 3.1 and 3.2.

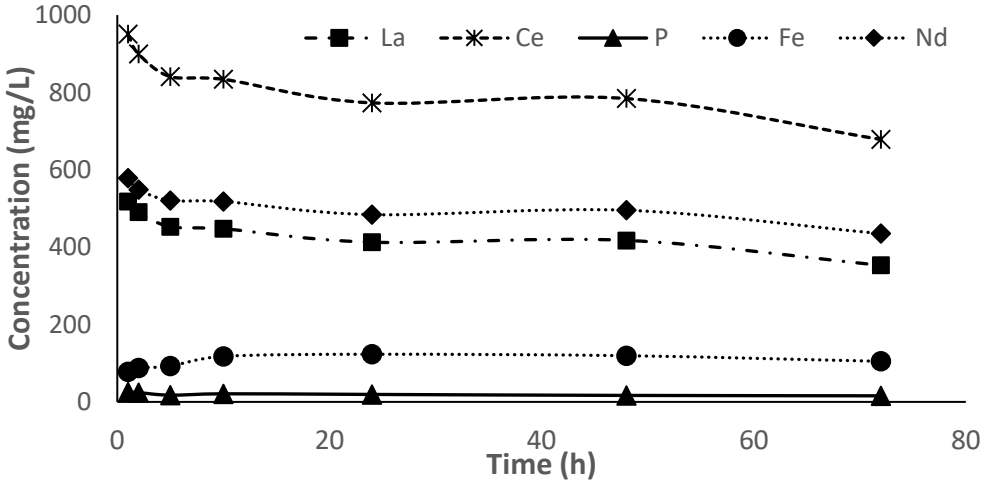

Figure 3.1: Leaching pre-treated monazite concentrate (30% removal) with 0.1 M citrate (100 g/L solids, 500 rpm, pH 10 and 25°C)

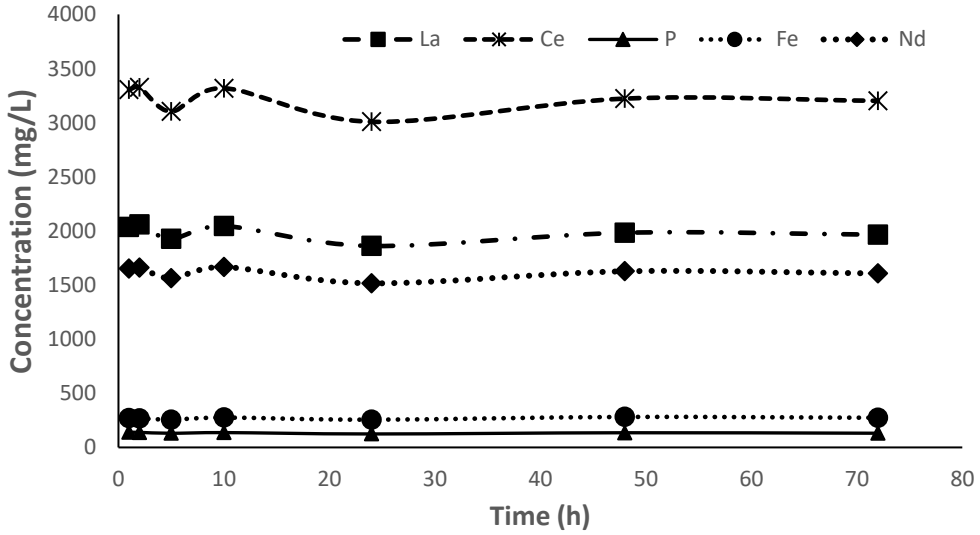

Figure 3.2: Leaching pre-treated monazite concentrate (30% removal) with 0.1 M EDTA (100 g/L solids, 500 rpm, pH 10 and 25°C).

The REE concentration in the citrate (Fig.3.1) peaks at the first measurement (1 h) and decays over time. The decay in REE concentration is similar to the trend observed in the study of Lapidus & Doyle (2015b), predominantly for Ce and Nd in solution with organic acids. This instability is a concern for subsequent processing as significant losses may occur with such rapid reaction rates. Interestingly, the iron concentration increased over time. Based on the findings during the oxalic acid conversion pre-treatment that consumption of the oxalate ions limited the reaction extent, it is possible that a similar mechanism is occurring here in which REE complexes are breaking down and the oxalate is forming iron complexes. There is thus an equilibrium that is initially not reached due to the solubility, and thus rapid dissolution, of the REE oxalate species in citrate. The rapid dissolution of REEs displays the effectiveness of the conversion stage compared to direct treatment of the monazite concentrate with the same lixiviants, which produced very slow leaching with minimal overall extraction.

Conversely, in the EDTA system (Fig. 3.2), while the highest concentration was also achieved in the first hour, it remained almost constant through time. Furthermore, EDTA achieved three times the REE recovery of citrate, but with a similar increase in the concentrations of impurities (P and Fe). This suggests a direct link between REE and impurity dissolution in this reaction, perhaps due to small amounts of Fe and P associated with the oxalate salts generated in the conversion stage. The greater recovery with EDTA is attributed to the vastly greater stability of the REE-EDTA complexes (K_1 = 16.6 (Nd)) as opposed to citrate (K_1 < 5 (Nd)), which also have limited solubility. Due to the speed of the reactions, the leaching time was set to a maximum of 1 hour for subsequent experiments with EDTA.

The fact that Nd is leached to a greater extent in both systems than the more prevalent, but less valuable, metals displays a level of selectivity above simply preferential leaching of the REEs over impurity elements. The difficulty discussed above in separation and purification of the individual elements leads to the conclusion that any selectivity in the extraction stage, particularly in concentrating Nd, represents a significant potential value to downstream processing. One driver of this result lies in the difference in stability constants between the various elements and oxalic acid. The reported constant of the Nd complex with oxalate (K_1 = 7.21) is higher than that for the respective Ce complex (K_1 = 6.05) (Sillen & Martel, 1964). As the extent of the conversion reaction governs the proportion of the element to be released upon secondary leaching, this difference is significant.

Directly comparing the release of REEs achieved in the EDTA leach of the pre-treated concentrate to the proportion of phosphorus released in the oxalic acid conversion stage it is clear that these are directly related. Conversion experiments conducted at various temperatures that achieved different levels of phosphorus release showed comparable variance in the levels of REE recovery in the EDTA leach (Fig. 3.3). This indicates that a primary limiting factor in REE extraction under these conditions is the effectiveness of the pre-treatment stage. An interesting point of note is the fact that the REE dissolution in EDTA is generally greater than the proportion of phosphorus released in the conversion stage. This observation may relate to some retention of dissolved phosphorus, either through adsorption or re-precipitation, in stage 1 may occur.

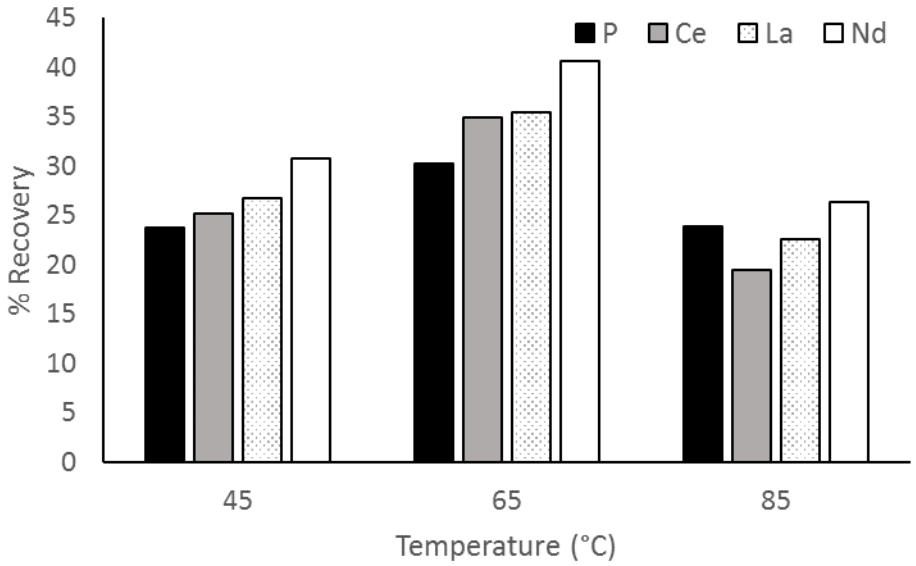

Figure 3.3: Recovery of phosphorus (first stage oxalic 0.8 M, S/L: 0.1, 500 rpm, pH 1, 10 hours at various temperatures) and REEs (second stage EDTA 0.1 M, S/L:0.1, 700 rpm, pH 10, 5 mins at 25°C)

The pH of the EDTA solution was varied between 6 and 10 with other parameters kept constant (0.1 M, S/L:0.1, 700 rpm, 5 minutes residence time and 25°C), which showed a significant impact to increasing the alkalinity of the solution (Fig. 3.4). This result is supported by the thermodynamic equilibrium between the oxalate and EDTA species as shown in Figures 3.5-3.7.

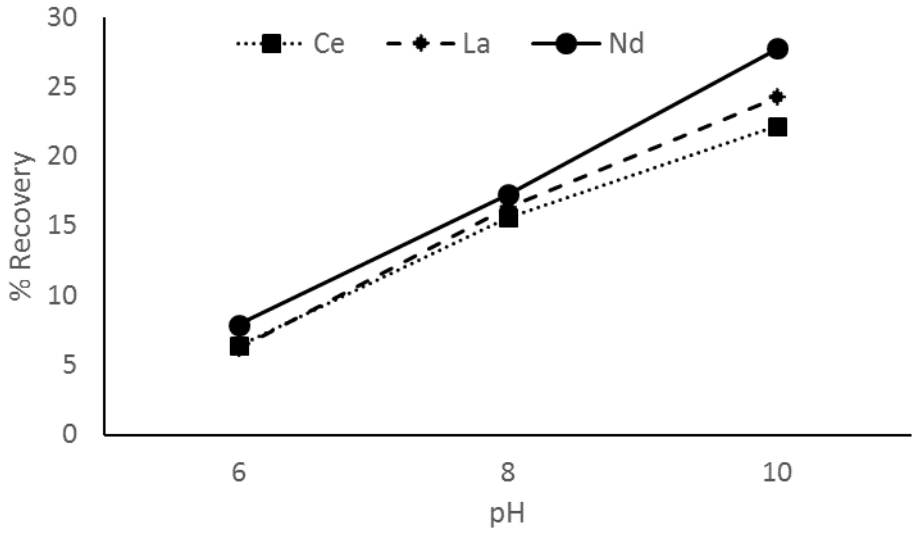

Figure 3.4: Recovery of REEs (EDTA 0.1 M, S/L: 0.1, 700 rpm, 5 mins at 25°C) at pH 6, 8, 10 from pre-treated monazite concentrate (29% removal, oxalic 0.8 M, S/L: 0.1, 500 rpm, pH 1, 72 hours at 25C)

The proposed reaction (Eq. 3.1) describing the dissolution of the rare earth oxalate from the pretreated monazite in an EDTA solution follows that given by Misumi & Taketatsu (1959). This suggests a combined RE-EDTA-oxalate is produced in this reaction.

$$RE_2(C_2O_4)_3 + 2HY^{3-} \xrightarrow{\text{yields}} 2(RE\ H\ YC_2O_4)^{2-} + (C_2O_4)^{2-} \quad (3.1)$$

Speciation diagrams were prepared using the Medusa software package (Puigdomenech, 2013) and its Hydra database (Fig. 3.5-3.7). As data for the proposed mixed REE-EDTA-oxalate compound was not available only the pure REE oxalate and REE EDTA compounds were considered. While this does not perfectly describe the system, the influence of both oxalate concentration and pH is demonstrated even at high concentrations of oxalate the EDTA solution complex is favoured above ~pH 7.5. Therefore, at pH values near the transition point, the reaction will reach equilibrium and stop as EDTA ions are consumed in the dissolution and oxalate ions are released. The greater extent of Nd release with respect to Ce and La is also suggested as the transition point between the oxalate and EDTA species occurs at a lower pH value.

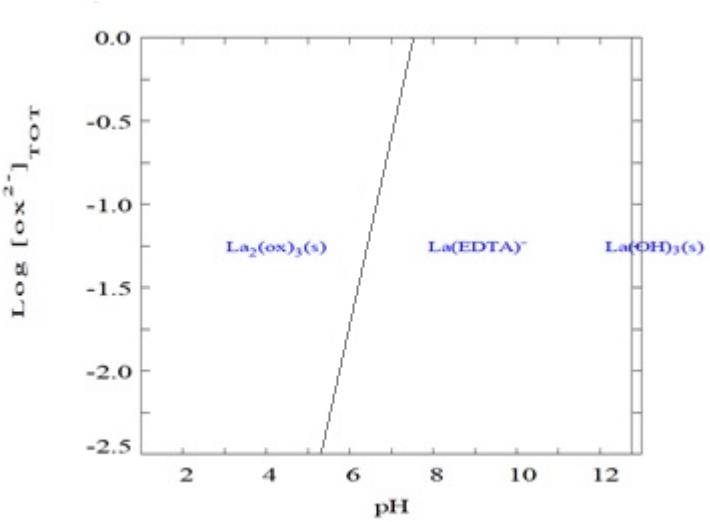

Figure 3.5: Speciation diagram for lanthanum as function of oxalate concentration and pH. Conditions: 0.055 mol La^{3+} and 0.1 mol EDTA per litre of solution at 25°C

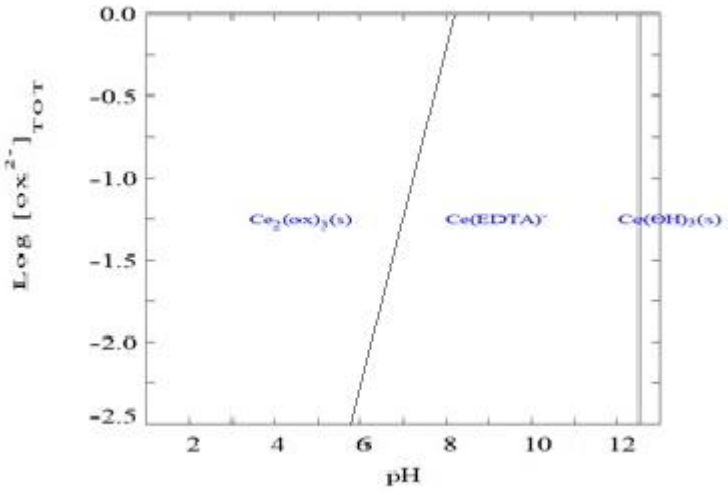

Figure 3.6: Speciation diagram for neodymium as function of oxalate concentration and pH. Conditions: 0.0906 mol Nd^{3+} and 0.1 mol EDTA per litre of solution at 25°C

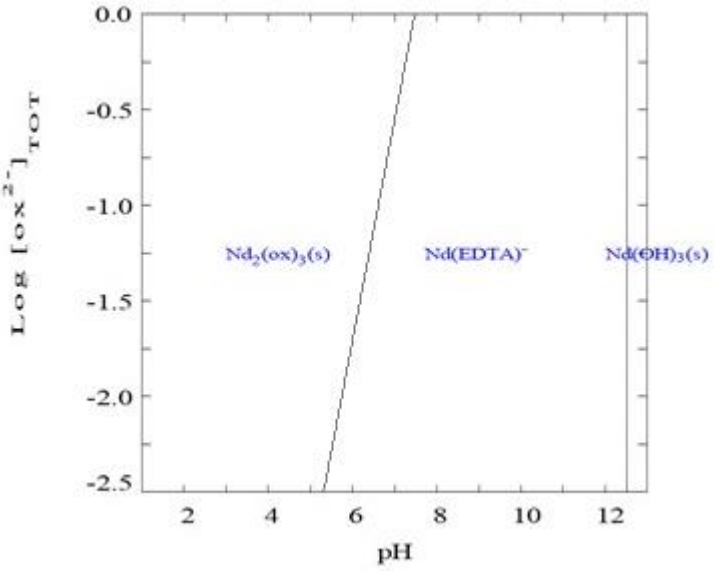

Figure 3.7: Speciation diagram for neodymium as a function of oxalate concentration and pH. Conditions: 0.0367 mol Nd^{3+} and 0.1 mol EDTA per litre of solution at 25°C

The stirring speed displays a moderate impact on REE dissolution in EDTA at ambient conditions (Fig. 3.8). The higher agitation speed resulted in concentration increases of between 10 and 20% for each of the rare earths in the PLS. The slightly elevated impurity levels suggest the additional rotation speed aids in the dissolution of all constituents of the pre-treated concentrate.

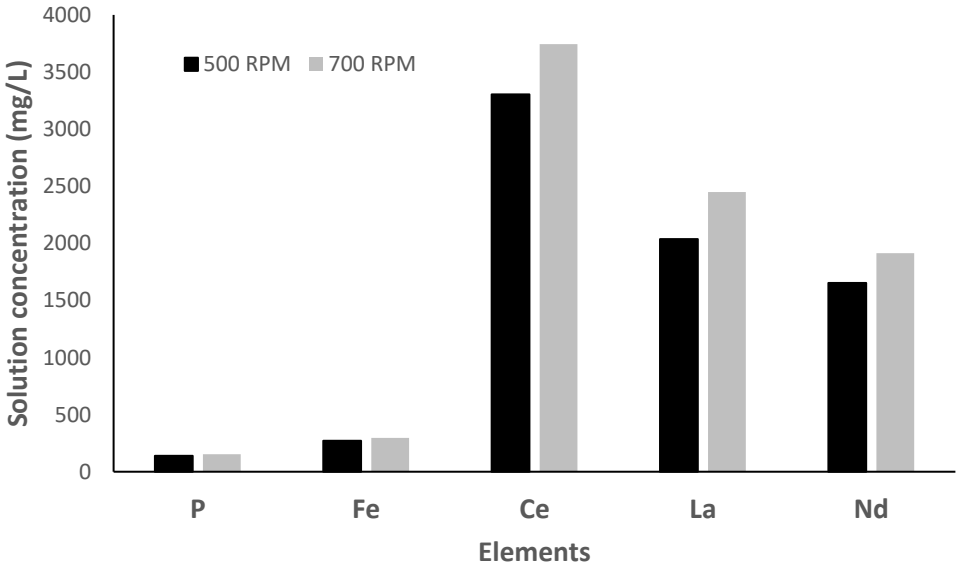

Figure 3.8: Leach solution concentration of pre-treated monazite concentrate (33% removal) 0.1 M EDTA for 1 hour pH 10 at 500 and 700 rpm and 25C

It was noted in chapter 2 that elevated temperature (65°C) greatly increased the rate of phosphorus release in the conversion leach. However, increasing the temperature to 85°C decreased the maximum release value due to consumption of the oxalate by the competing iron dissolution reaction. As can be seen in figure 3.10, nearly 50% of the Nd and more than 40% of the Ce and La were recovered from the sample treated with oxalic acid at 65°C for just 10 hours. This is greater than that achieved in 72 hours of the conversion stage at 25°C, while still not releasing a significant proportion of iron into solution. Again, the concentration peaked within the first 5 minutes of the experiment, remaining relatively consistent thereafter. The speed of this reaction also provides the opportunity to avoid any unfavourable side reactions such as a slow release of impurities. From Figure 3.9 (50g/500mL) 5 mins leaching: P, 23.5 mg/mL; Ce, 4431 mg/mL; La, 2659.8 mg/mL; Fe, 85.8 mg/mL; Nd, 2150.8 mg/mL; Y 57.9 mg/mL.

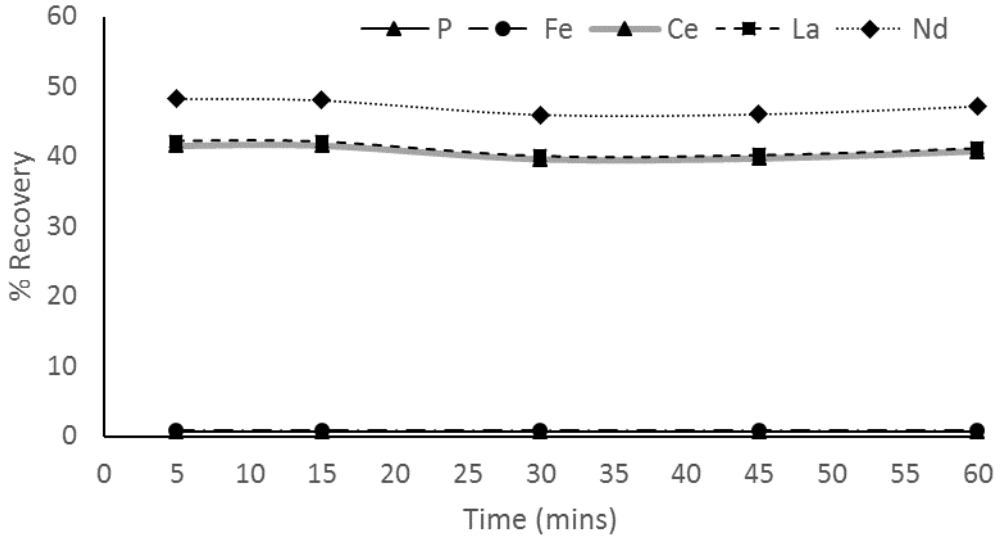

Figure 3.9: Recovery of REEs and impurities 0.1 M EDTA for 1 hour, pH 10, 700 rpm and 25°C from pre-treated monazite concentrate (37% P removal, 0.8 M, S/L: 100 g/L, pH 1, 65°C and 10 hours)

Once a single pass of both the oxalic acid conversion leach (85°C) and EDTA secondary leach were completed (achieving 21.9%, 22.8% and 27.4% recoveries respectively for Ce, La and Nd). The results of the second EDTA pass (Fig. 3.10) shows a continuation of the conversion and leaching process, leading to a total of more than 50% of the Nd being recovered from the monazite sample and more than 40% of both Ce and La.

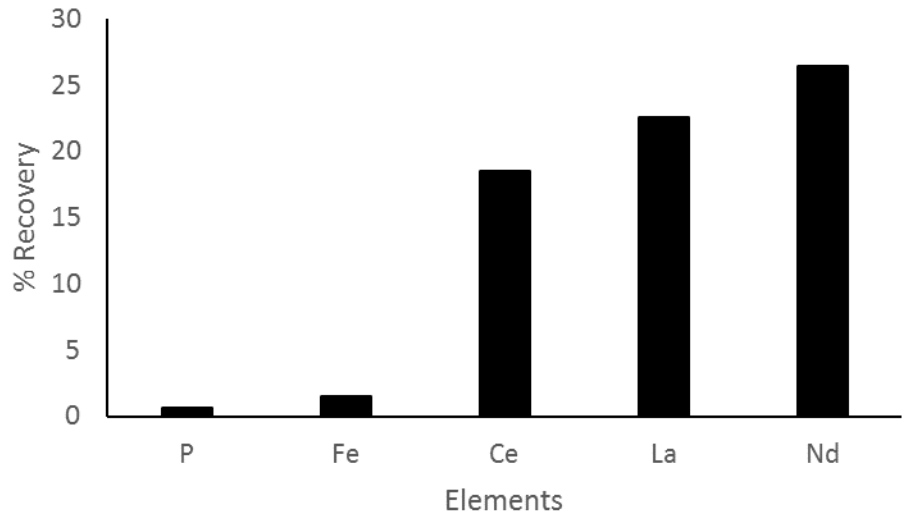

Figure 3.10: Recovery of REEs and impurities 0.1 M EDTA second leaching for 5 min, pH 10, 700 rpm and 85°C from pre-treated monazite concentrate (20% P removal, 0.8 M, S/L: 100 g/L, pH 1, 85°C and 10 hours)

The addition of further oxalic acid to the conversion leach was previously shown to continue the reaction after the reaction had stopped in the first pass. An experiment was conducted treating monazite concentrate under otherwise standard conditions (0.8 M oxalic acid (initial), pH 1, 65°C, 100 gL^{-1} solids) but with a further 0.8 $molL^{1}$ of oxalic acid added after 5 h of reaction time. The reaction was allowed to proceed for 24 h to allow the reaction to reach equilibrium. The residue was then leached at ambient temperature in 0.1 M EDTA for 5 min (pH 10, 50 gL^{-1} solids) (Fig. 3.11). As can be seen an enhanced proportion of REEs are obtained, displaying the fact that addition oxalic acid applied in the conversion stage does continue the reaction. Given the recoveries are less than twice that obtained without the additional reagent, it appears that the efficiency of the process decreases with the additional oxalic acid. These results also correspond well with the phosphorus recovery from the conversion stage of 51.9%. The results presented in figures 3.10 and 3.11 display that multiple options exist for maximizing the total REE recovery in this treatment and further managing the release of specific elements.

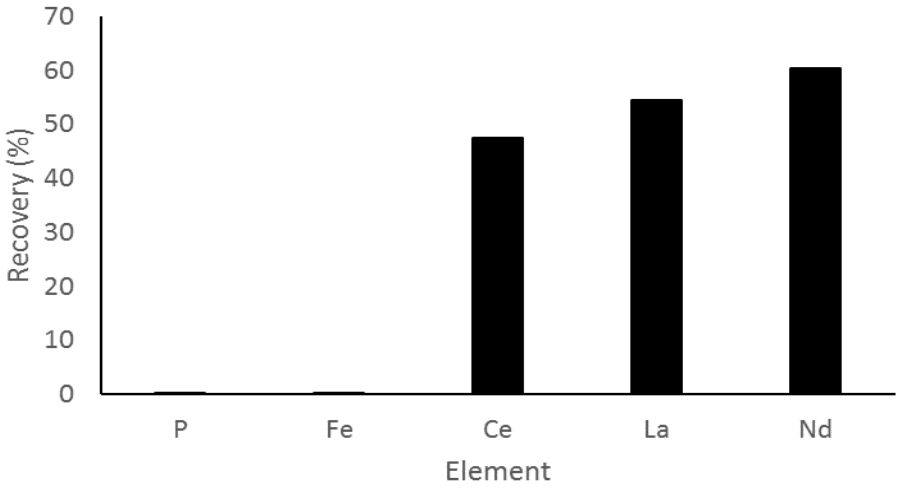

Figure 3.11: Recovery of REEs and impurities during EDTA leaching of the reside obtained from the conversion leach stage that employed the addition of further oxalic acid at 5 h (52% P removal)

3.3.3 Tailings water

Most of the mine sites are located in remotes areas where the water supply is limited and expensive. Several metallurgical processes (such as flotation) produces huge amount of tailings water which can be recycled. Recycling tailings water not only decrease the cost of operation but also reduce the volume of tailings water and tailings ponds maintenance.

Monazite pre-treat concentrate under the effect of EDTA using tailings water reported a remarkable decline in recovery of REEs (~ 66% decrease) (Figure 3.12). Several elements are present in tailings water and magnesium and calcium are the most prolific minerals which define a hard water. The presence of Ca^{+2}, Cl^{-} and Mg^{+2} may be in competition with the REEs which produce a low recovery of REEs in solution. Equation (3.2) described the chemical equation. No further experiments were carried out to determine the mechanism because it is a secondary nature in the research project.

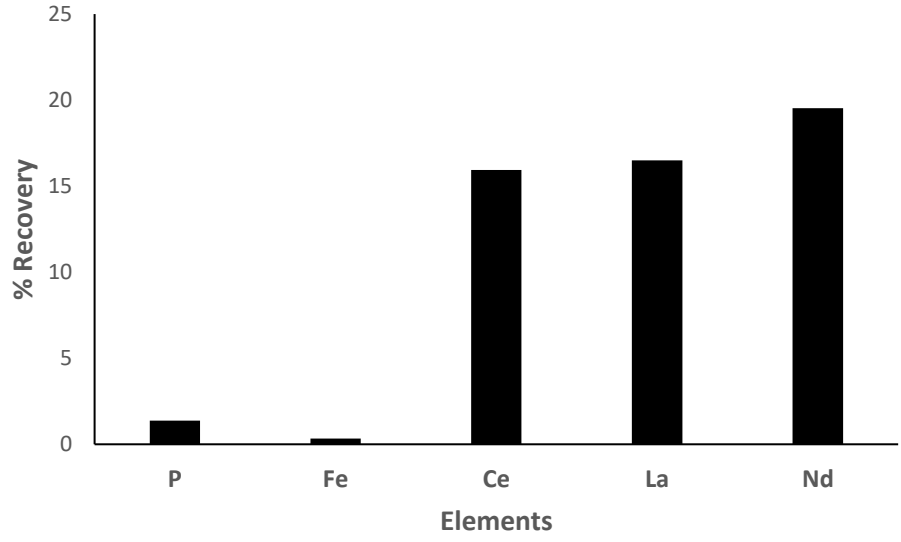

Figure 3.12: Recovering of REEs and impurities 0.1 M EDTA for 1 hour pH 10 700 rpm using tailings water and 25°C

3.4 Conclusions

While, citric acid and EDTA reported a significant release of REEs from the pre-treated monazite concentrate, EDTA performed significantly better. The release of impurities (P and Fe) remained below 1% in both acids which emphasized the selective leaching. Remarkably, the leach of the REE oxalate species was complete within 5 minutes, even at ambient temperature. The stirring speed had a significant effect on the dissolution of REEs, increasing solution concentrations by 10 to 20%. The acceleration of phosphorus release observed at elevated temperatures correlated to more rapid REE conversion as expected. When the conversion was conducted at 85°C the additional iron release resulted in poorer REE recovery in the secondary leach.

The amount of phosphorus released in the first stage of the process has a strong influence in the recovery of REEs in the second stage. Moreover, the extraction of REEs under the effect of EDTA is strongly pH dependent. The release of REEs decreased when the temperature increased in EDTA. It seems the compounds at high temperature diminish the stability of the RE-EDTA-oxalate complex, potentially creating other insoluble compounds such as hydroxides. Furthermore, the second pass of the EDTA leach has shown that REEs continued to be released from the residue. It suggests that the extraction stops due to the consumption of RE oxalate created in the first stage of the process. The impact of employing tailings water was the decrease of recovery of REEs which has the same pattern as for oxalic acid. Thus, the use of tailings water in formation of RE-EDTA-oxalate complex is uncertain to the results obtained. Further experiments need to be performed.

CHAPTER 4.
RARE EARTH HYDROXIDE AND PRECIPITATION

4.1 Introduction

Several sections of this chapter are constituted by the publications

- Treatment of monazite by organic acids II: Rare earth dissolution and recovery. 2018. Lazo, D., Dyer, L., Alorro, R., Browner, R. Hydrometallurgy, (179); 94 - 99
- Solubilisation of monazite in organic acids. Lazo, D. Dyer, Alorro, R. European Metallurgical Conference, Leipzig, June 2017

The formation of rare earth EDTA oxalate (RE EDTA oxalate) is the second stage of the new process described in the previous chapter, where the RE EDTA oxalate is formed in solution from RE oxalate salt. In our research, the RE EDTA oxalate needs to be in more amenable species so it can be feed in the separation stages.

A key requirement for this process to have a potential application is the ability to separate and purify the extracted elements. The simplest method was to attempt to produce a material or stream that can be treated with conventional technology. Standard conventional processing converts the rare earth oxalate precipitated from the sulphuric acid leach solution into a hydroxide to feed the solvent extraction circuit.

The common approach to separate REEs is via solvent extraction (SX). Now, the oxalic acid has demonstrated that the creation of ligands or chelate denoted an important property of organic acids to precipitated rare earth oxalates. Therefore, if a hydroxide could be generated from the EDTA leach solution, the process could then use conventional REE solvent extraction.

Moreover, this innovative method can replace the conventional extraction method without any significant change in the overall current process. It is important to mention that the same separation process, solvent extraction (SX) in most cases, can still be applied. In fact, the SX separation process can be simplified with the PLS obtained by this new method.

The ability to produce a RE hydroxide also allows it to replace conventional extraction while still employing the same separation technology.

4.2 Experimental

4.2.1 Materials

The primary component is the solution RE EDTA oxalate using ionized water which was created in the previous stage and described in Figure 3.4 at 25°C.

The secondary component is the solution RE EDTA oxalate using tailings water which was created in the previous stage and described in Figure 3.12.

The presence of Th and U in the ore are very low. The monazite concentrate is not considered radioactive because the low proportions of Th and U. Aside of the research project, a Japanese student has had the chance to measure the radioactivity in the concentrate in January 2017 in Sapporo, Japan and it was not considered radioactive.

4.2.2 Methods

In order to generate a REE hydroxide from this system, a sample of RE-EDTA- oxalate leach solution (50 mL) was combined with 100 mL of 2.5 M NaOH (pH~13.8) in a 250 mL round bottom flask and heated in an Analog Heating Mantle PTHW250at 95°C for an hour. The solution was filtered and the solid washed with deionized water. The solids were dried, coarsely grounds and analyzed by XRD and the solution analyzed by ICP-OES. Some elements were assayed in the majority of the tests.

The previous chapter describes the method of creating a RE oxalate salt from PLS of an acid roast-water leach treatment of the monazite concentrate. A RE hydroxide for comparison to that generated from the organic acid treatment was formed by adding the prepared oxalate solids to 100 mL NaOH (2.5 M) in a 250 mL round bottom flask and heating in an Analog Heating Mantle at 95°C for an hour. The solution was filtered and he residues were washed with deionized water. The solutions were analyzed by ICP-OES and the solids by XRD.

Further experiments with the formation of RE hydroxide was conducted employing tailings water (under the same set up conditions at 25°C from the mine site) and the composition of the tailings water can be observed in Table 2.2. In the experiment, the slurry was filtered and the solids were washed with deionized water.

4.3. Results and discussion

4.3.1 Using deionized water

The residue of the hydroxide preparation was analyzed by XRD and compared with the peaks obtained using the solution from conventional acid roasting treatment (Fig. 4.1). These were also compared to the RE oxalate phase produced from the acid roast system to ensure that full conversion had been achieved. This was done as the mineral databases available do not contain any RE oxalate or hydroxide phases. There is no evidence of the oxalate peaks in the hydroxide sample suggesting a complete conversion had been achieved and that the sample was viable for comparison. The precipitates had very similar structures, confirming the successful creation of rare earth hydroxide from the EDTA leach solution.

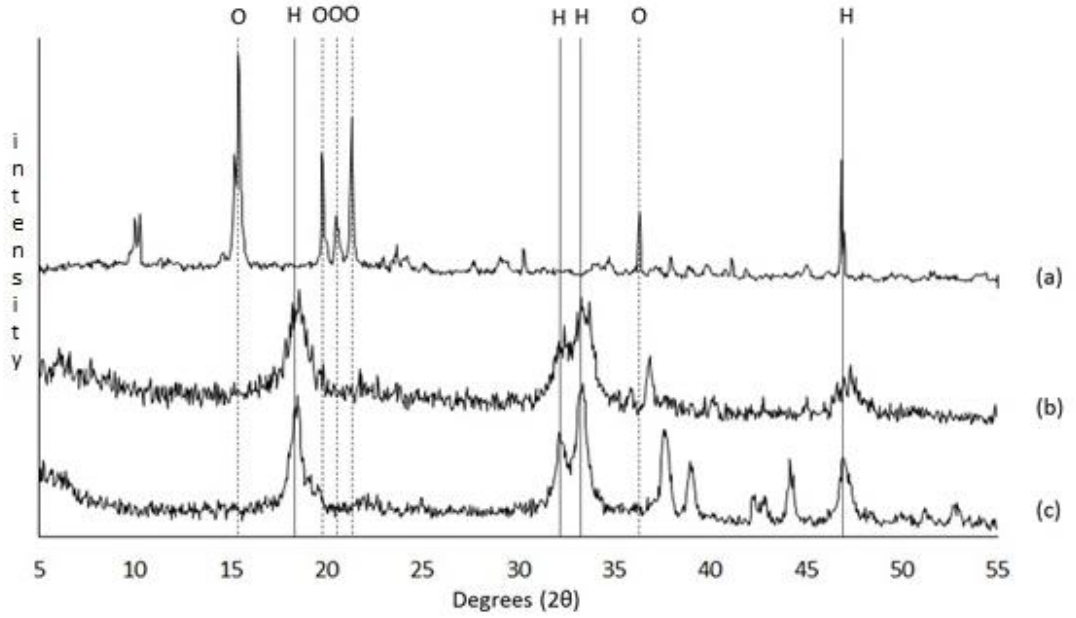

Figure 4.1: X-ray diffractograms of samples obtained from (a) the REE oxalate (b) subsequent REE hydroxide generated from sulphuric acid roast-water leach solution and (c) the RE hydroxide produced from the EDTA leach solution.

Furthermore, it can be observed that the creation of RE hydroxide was supported by the speciation diagrams in Figures 3.5-3.7. They displayed that RE hydroxide can be achieved by raising the pH to above ~13, but to do so would consume significant amounts of reagent. Thus utilising elevated temperature to favour the hydroxide formation at lower pH levels (as is done in industrial practice converting RE oxalate to hydroxide) is the preferred option. XRF analysis of the hydroxide precipitates formed from both systems showed very similar compositions, with total REE contents of more than 50 %.

4.3.2 Using tailings water

Water supply is scarce and expensive where most the mines are located in regional areas. Recycling tailings water is an important process which lead to reduce the utilization of fresh water, decreasing production cost, reducing tailings water volume and maintenance of tailings ponds. RE hydroxide formation was performed using tailings water. NaOH 2.5 M was prepared using tailings water. The solution was filtered and the residue washed with deionized water. The residue was analyzed by XRD (Figure 4.2).

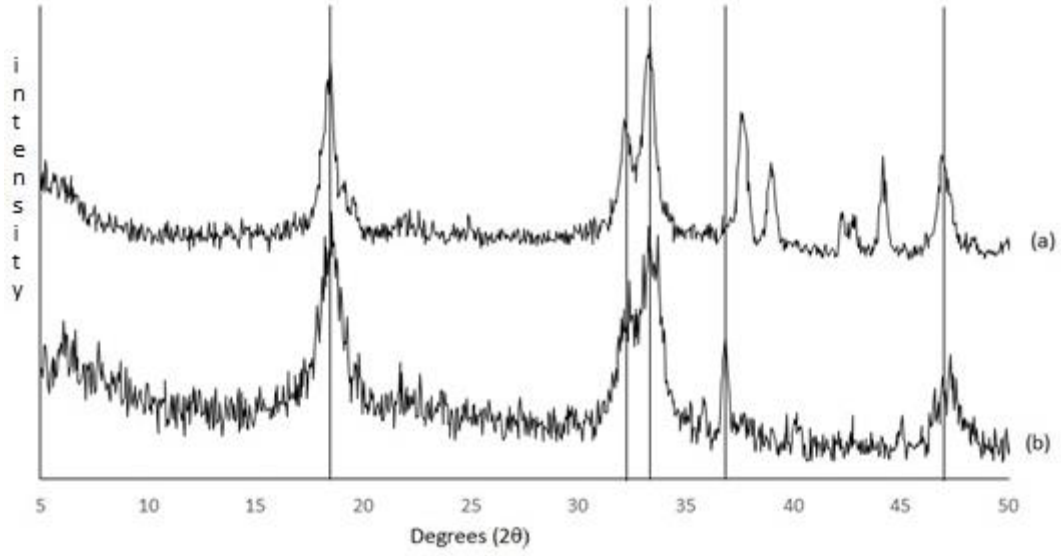

Figure 4.2: XRD diffractograms generated from the rare earth hydroxide (a) hydroxide formation using tailings water (b) from the acid roasting process

The conversion from RE EDTA oxalate to RE hydroxide using tailings water shown the capability of using tailings water. It could have a great impact in the cost/benefit of the process. RE hydroxide was able to be produced from the leach residue allowing this process to be applied to conventional solvent extraction.

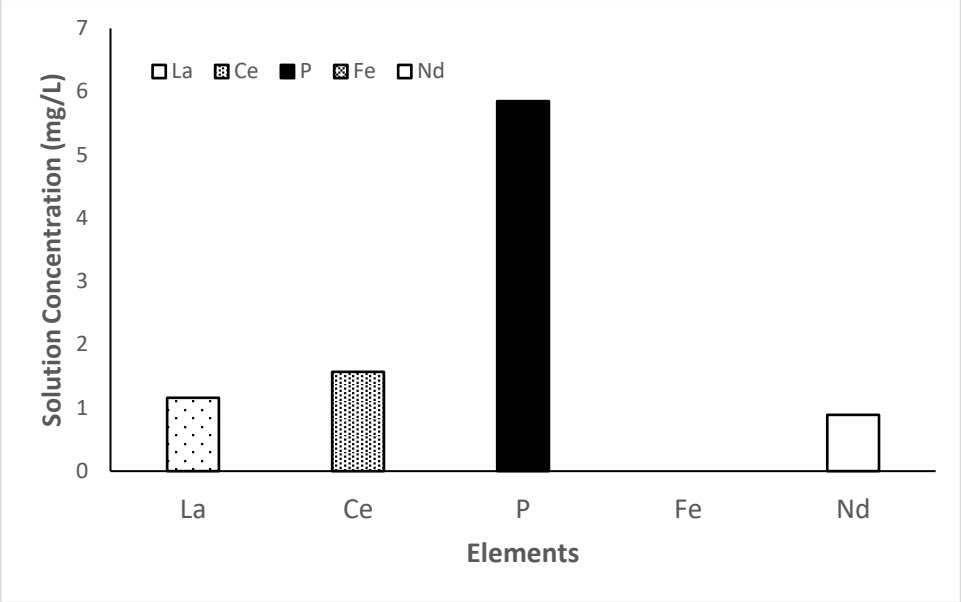

Figure 4.3: REEs in the solution after precipitation as RE hydroxide

Fig. 4.3 shows the amount of REEs in solution after being precipitated as RE hydroxide. The low quantities of REEs displays a great success in precipitation of RE-hydroxide. The high amount of P among the REEs shows that the precipitation is very selective. The presence of Fe is almost null due to the selectivity of the recovery of EDTA in the previous stage. Using tailings water in this stage is noteworthy to mention and add flexibility in the process.

In Appendix 2, there is more information related to tailings water study.

4.4 Proposed Flowsheet

Figure 4.4 contains a proposed flowsheet for the development of this treatment regime. Regardless of the effectiveness of the REE extraction and recovery stages, the viability of any potential process also rests with the ability to recycle reagents and solutions including impurity removal and potential by product formation. For example, given the strong recovery of phosphorus in the oxalic acid leach, the generation of phosphate products such as fertilisers represent significant opportunities for additional value and a more robust process. The primary stages, the oxalate conversion leach, the EDTA REE extraction and subsequent generation of a hydroxide have shown success at this level.

In the first stage, the monazite concentrate is converted to RE oxalate which precipitated under the effect of oxalic acid. The process can be accelerated with high temperature and the addition of fresh oxalic acid increases the conversion to RE oxalate. It has been observed that the efficiency of this reaction is acutely impacted by water quality. A cooling system needs to be added (from 65°C to 25°C). During the second stage, the RE oxalate precipitated was extracted into solution under the effect of EDTA and the creation of RE EDTA oxalate in solution. The extraction of REEs under the effect of EDTA is very selective because the amount of impurities in the solution is very low. This stage is able to tolerate higher dissolved solid contents, displaying resilience to decreased water quality. The third stage created RE hydroxide from the solution RE EDTA oxalate. This whole process can replace the conventional extraction method (acid roasting) without any significant change in the overall current process. It is important to mention that the same separation process, solvent extraction (SX) in most cases, can still be applied as the product fed to SX has been generated from the PLS. In fact, the SX separation process may be simplified if a degree of selectivity can be achieved earlier in the process.

Another opportunity has been identified to use these reagents from the mine site monazite concentrate. Some low-grade ores are discarded into stockpiles in the mine site before the process of beneficiation is conducted. These ores respond poorly to flotation and are thus not cost effective to treat with current technology at the present commodity prices. However, due to the benign nature of the reagents, their effectiveness at ambient temperature and the tendency for gangue minerals not to be leached to a significant degree, heap leaching using the proposed technology has been suggested. Therefore, research is necessary to confirm the potential of this method for heap leaching of low-grade ores.

However, the whole process requires optimisation and the ancillary processes investigated. Of primary concern are the oxalate recovery due to the high consumption in the conversion leach, the alkalisation stage and potential phosphate product generation. The leaching time (10 hours at 65°C) in the creation of RE oxalate (first step) would ideally be decreased in industrial scale. Second and third step are rapid and efficient. Important parameters for large scale operation would be the cost of the reagents: oxalic acid, EDTA, NaOH depending on consumption and recycling and potentially power to maintain temperatures.

The conventional rare earth extraction technologies, while often highly effective, have several associated issues from high cost, reagent and energy consumption to hazardous material handling and by-product generation. It is not within the bounds of conventional techniques to properly address these issues with simple process optimisation or additional infrastructure such as scrubbers. Therefore, alternative processes hold the key to cleaner, cheaper rare earth processing allowing for a more competitive international market.

The conventional methods of extracting REEs have several disadvantages:

a. High concentration of corrosive reagents.
b. The potential to produce hazardous gases (sulphur dioxide - SO_2, sulphur trioxide – SO_3, hydrogen fluoride – HF, etc.).
c. The processes are undertaken at high temperature.
d. The high electricity consumption cost.
e. The cost of maintenance due to the extreme conditions for operation.

Table 4.1: Advantages and disadvantages of proposed flowsheet

Advantages	Disadvantages
Short time leach EDTA	Long reaction
Final product can feed the SX without any modification or addition of process	Consumption of an expensive sodium hydroxide
Low maintenance cost	Leaching efficiency is not higher than 75%
Non-aggressive method	Three step independent strategy
Creation RE hydroxide in less than hour	
Recycling of reagents	
Non- aggressive effluents	

This new approach can replace (without significant modification) the most common conventional extraction method (acid roasting). It is important to mention that the same separation process, solvent extraction (SX) in most cases, can still be applied as the product fed to SX has been generated from the PLS. In fact, the SX separation process may be simplified if a degree of selectivity can be achieved earlier in the process.

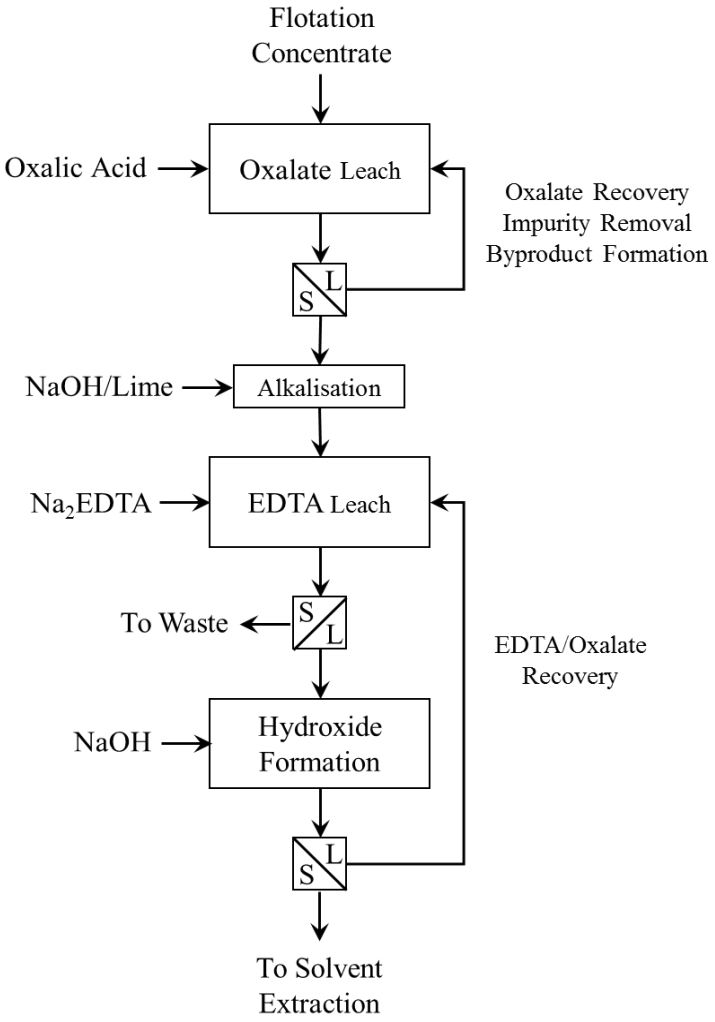

Figure 4.4: Proposed flowsheet for the treatment of monazite

4.5 Conclusions

A RE hydroxide was successfully generated directly from the EDTA leach solution suggesting that the treatment would be able to feed conventional solvent extraction. This is based on the fact that RE hydroxides are used in conventional processing as a feed material for solvent extraction circuits. Such an achievement greatly improves the potential viability of developing an applicable process. Tailings water used to test the impact of dissolved solids on the process showed a marked decrease in phosphorus release, suggesting a significant decrease in monazite conversion. This novel approach can replace the conventional process (acid roasting) without any important modification

in the current process and feed for the separation process (solvent extraction) is generated by the RE hydroxide. In fact, this novel method is the first non-aggressive method to be used to extract REEs from monazite concentrate.

The effectiveness of using tailings water in the creation of RE hydroxide would be a significant issue for scale up. Recycling tailings waters would have an important impact in the feasibility of the proposed flowsheet.

CHAPTER 5.
COMPARISON OF THE REACTIVITY OF XENOTIME AND MONAZITE IN VARIOUS SYSTEMS

5.1. Introduction

The bulk of this chapter is constituted by the publication (under review) " Comparison of the reactivity of xenotime and monazite in various systems". Lazo, D., Dyer, L., Alorro, R., Browner, R. Mineral Engineering (under review).

Earlier research performed by this team addressed the initial success of using organic acids in the extraction of rare earth elements in monazite, a rare earth phosphate mineral like xenotime. Lazo et., (2017) shown that oxalic acid enhances the dissolution of phosphorus and the creation (and precipitation) of RE oxalate. The experiments performed under no extreme conditions which is the first metallurgical process of this type. Lazo et al., (2018) demonstrated the second part of the process where described the recovery of REEs and subsequent formation of RE hydroxide. RE hydroxide is the feed of solvent extraction separation method. Also, the nonexistence of hazardous gases and tailings demonstrated that it is a friendly environment process.

Mechanochemical treatment involves physicochemical and chemical changes in the material produced by applying mechanochemical energy (Baláž, 2003, Baláž et al., 2005). When several substances are milled together, mechanochemical solid phase reactions might arise during the welded interfacing (Kim et al., 2009). Increased reaction rate, formation of water soluble ability, lower reaction temperatures and increased dissolution are the most important advantages of mechanochemical treatment (Baláž et al., 2005).

5.2. Materials and methods

5.2.1 Mineral characterization

The composition of xenotime concentrate employed is given in Table 5.1. The concentrate was dried out and the particle size analysis was performed by a Malvern Mastersizer 3000 using Hydro EV. The P_{80} of the concentrate was noted to be 87 μm. Some elements were assayed in the majority of the tests.

Table 5.1: Assay of concentrate

Element	Grade (wt%)	Element	Grade (wt%)
P	4.61	La	0.362
Y	9.09	Nd	0.651
Dy	1.57	Pr	0.132
Ce	0.86	Sm	0.395
Tb	0.2	Eu	0.075
Gd	0.936	Lu	0.091
Er	0.893	Yb	0.627
Ho	0.317	Tm	0.128

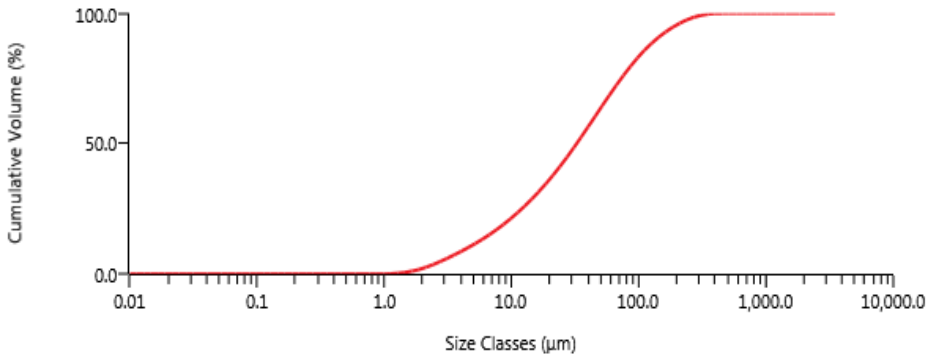

Figure 5.1: Average undersize particles xenotime

5.2.2 Methods

From earlier experiments (Lazo et al, 2017;2018) demonstrated that oxalic acid was able to increase the dissolution of phosphorus in monazite concentrate and precipitated the REEs. Subsequent, EDTA was able to recover the REEs from the residue. Xenotime is a rare earth phosphate like monazite. Therefore, the same screening experiments were carried out in xenotime concentrate to determine if oxalic acid or other organic acid are capable of solubilizing xenotime concentrate. The lactic, maleic, crotonic, sodium oxalate, sulphuric acids as well as sodium hydroxide used were all laboratory grade. The citric, gluconic, levulinic, mandelic, formic, acetic, tartaric, sodium sulphate and oxalic acid were analytical grade reagents.

The experiments were conducted in a 250 ml Erlenmeyer flask with a lid. Four parameters were tested: concentration of the organic acids, type of organic acid, pH and residence time at room temperature of 25°C. Solutions were analyzed by an ICP-OES (Agilent 5100 Synchronous Vertical View-SVDV).

5 g of xenotime was added in 50 mL of solution for each of the organic acids (two batches) 0.2 M in two Erlenmeyer flasks and stirred, one flask was set to pH 2 and the other to pH 5. Sodium hydroxide or sulphuric acid was employed to set up the pH. Once thoroughly combined, the flasks (with lids) were placed in an Incubator Shaker Labwit ZWY-211B for 24 hours at 100 rpm and 25°C. The mixture was filtered, the solid was washed with distillated water and the solutions were analyzed by the ICP-OES.

Then, another set of experiments were carried out with lactic, gluconic and mandelic acids with 5 g of xenotime (50 mL of organic acid, 0.2 M, pH 1 for 24 hours at 25°C) and put in an Orbital Shaker SS70 Chiltern Scientific.

The last set of experiments with oxalic, citric, tartaric and maleic acids, which reported the strongest dissolution of monazite (Lazo et al., 2017), was carried out with 5 g xenotime (50 mL of organic acid, a concentration of 0.2M, natural pH at 50°C). The four flasks (with lids) were placed in the Incubator Shaker described above at 50°C for 24 hours at 100 rpm.

Mechanochemical pre-treatment experiments were carried out to enhance the options of successful extraction of REEs using a Planetary Ball Mill (PBM). The study involved two stages. The primary milling stage involved xenotime concentrate mixed with sodium sulphate or sodium oxalate. 34.75 g of sodium sulphate (Na_2SO_4) was mixed with xenotime concentrate at a 1:1 molar ratio at 300 rpm. Samples were taken at 0.5, 1, 3 and 6 hours milling time. Next,

this experiment was repeated using 32.68 g sodium oxalate ($Na_2C_2O_4$) at 1:1 molar ratio and taking samples in the same amount of time. The secondary leaching stage where the sodium oxalate treated samples and sodium sulphate treated samples were leached employing sodium hydroxide and sulphuric acid respectively. 2 g of treated sample was mixed with its respective acid (1 M, 50 mL) for 3 hours and placed in a shaking table. The solutions were filtered and analyzed by ICP-OES.

5.3. Results and discussion

5.3.1 Screening tests at 25°C, pH 2 and 5.

Preliminary screening tests were performed to define the impact of several acids at pH 2 and pH 5 (Figs 5.2 and 5.4, respectively). Yttrium and dysprosium are the most abundant rare earth elements in xenotime. Moreover, the concentrations would indicate if the organic acids had selective complexation behavior with rare earth elements. The concentration of phosphorus was also measured to determine if the organic acids were capable of enhancing the solubilisation of phosphorus.

In the present study, the organic acids did not indicate enhanced solubilisation of phosphorus or REEs in xenotime concentrate in both cases (pH 2 and pH 5). (Fig 5.2 and 5.4). A previous study (Lazo et al., 2017) shown that oxalic, citric, tartaric and maleic acids had the ability to enhance dissolution of monazite in acidic conditions (pH 2) in significant quantities (Fig. 5.3). Although both minerals are rare earth phosphates, they reacted quite differently under the effect of the same acids and conditions.

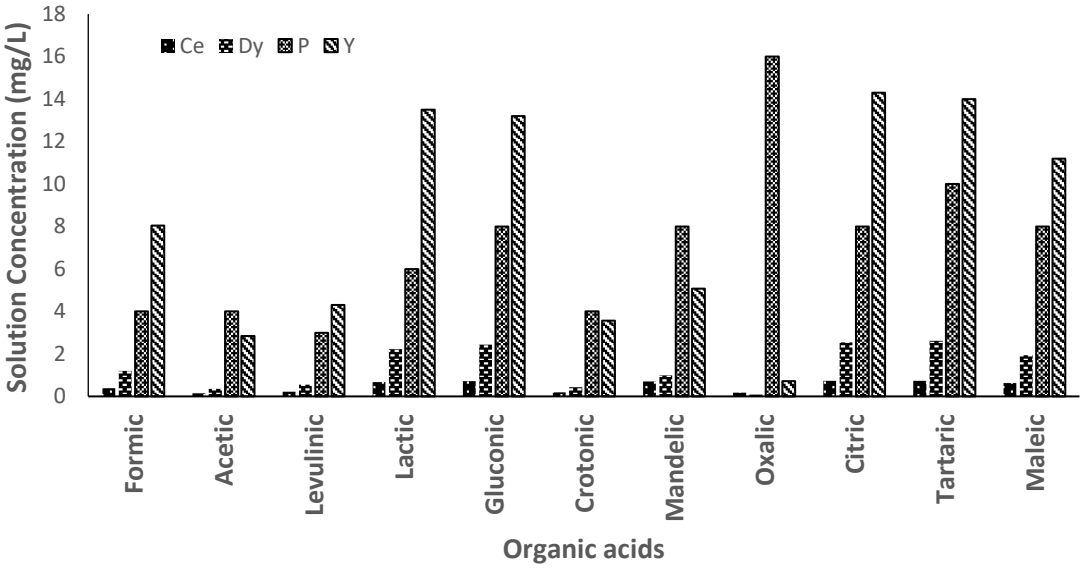

Figure 5.2: Leaching of xenotime for 24 hours 0.2 M at pH 2 and 25°C

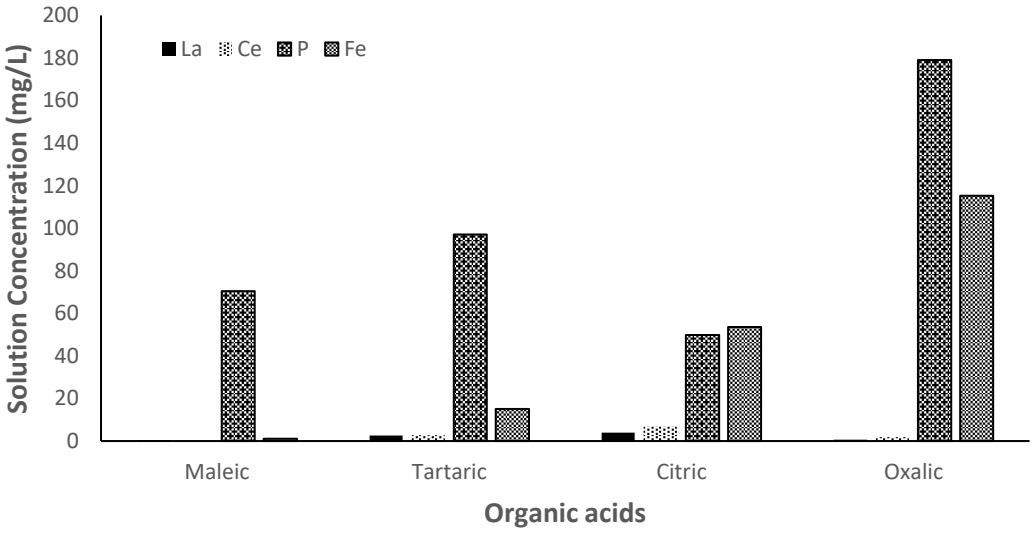

Figure 5.3: Leaching of monazite for 24 hours 0.2 M at pH 2 and 25°C (Lazo et al., 2017)

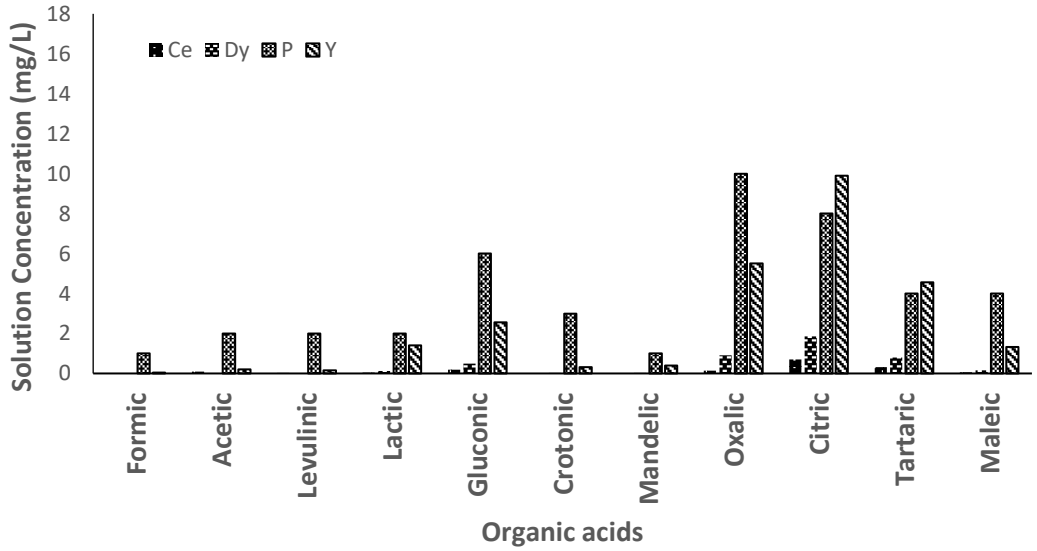

Figure 5.4: Leaching of xenotime for 24 hours 0.2 M at pH 5 and 25°C

5.3.2 Screening tests at 25°C at pH 1

Lactic, gluconic, mandelic acids were studied to find out the effect on xenotime at lower pH. The results have shown that there is not a crucial impact in the dissolution of xenotime. In fact, the results have shown a slight increase of dissolution but not a significant amount.

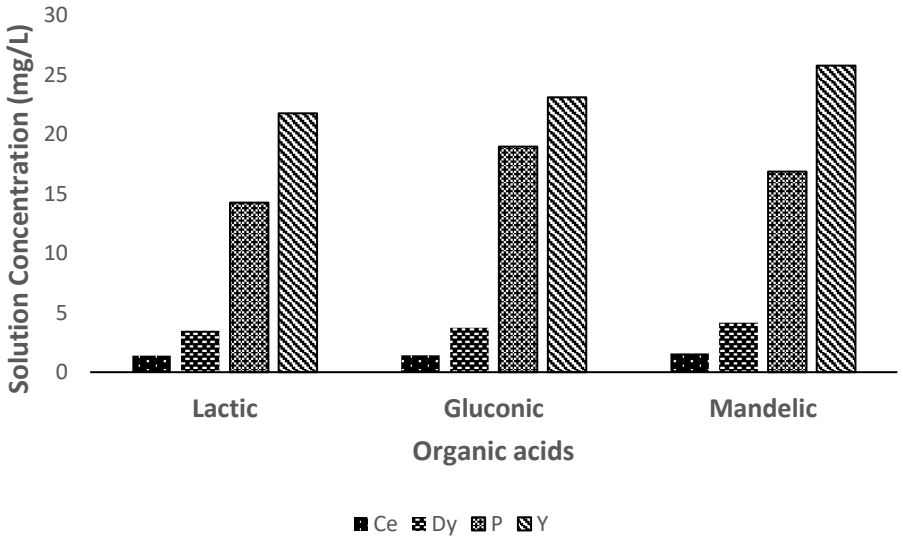

Figure 5.5: Leaching of xenotime for 24 hours at pH 1 and 25°C

5.3.3 Screening tests at 50°C at natural pH

Oxalic, citric, tartaric and maleic acids were studied to determine the effect on xenotime at a higher temperature and they were the strongest acids to solubilise phosphorus in monazite at 25°C (Lazo et al., 2017) (Fig. 3). The results indicated almost the same degree of solubilisation of xenotime registered at normal temperatures (25°C) in acidic conditions at pH 2. These results coincide with the findings in the oxalation stage in the method of processing monazite sands (Weltz & Smutz, 1958) where the temperature had no influence on the oxalate precipitation.

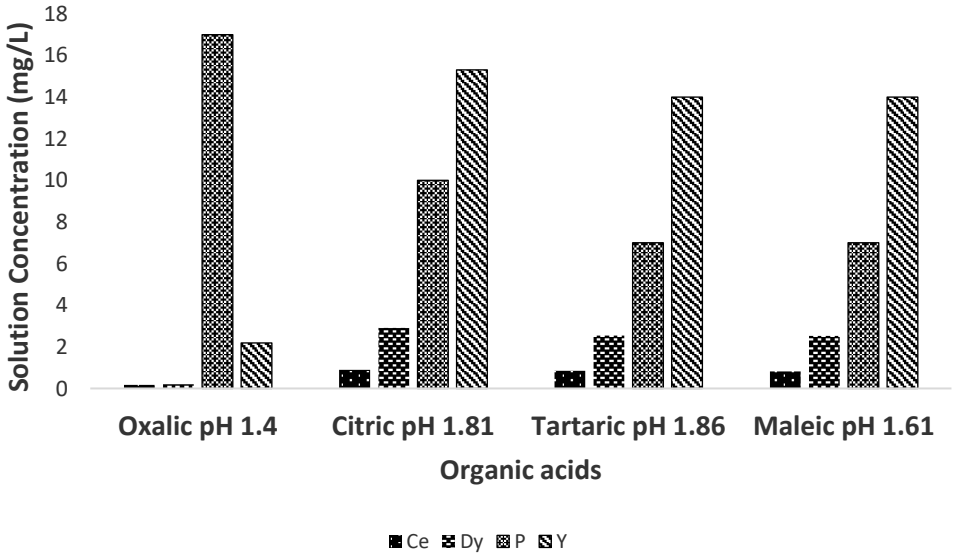

Figure 5.6: Leaching of xenotime for 24 hours 0.2 M at natural pH and 50°C

5.3.4 Mechanochemical treatment

The sample treated with sodium sulphate leached with sulphuric acid increased the dissolution of yttrium as long as milling time was increased (Fig. 5.7). The quantity of yttrium release is not significantly important, and it is not cost/benefit approachable.

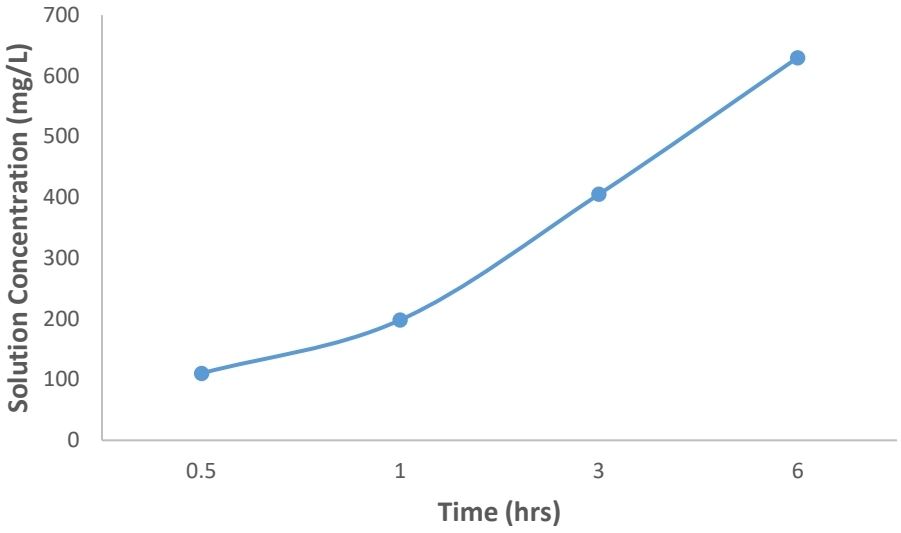

Figure 5.7: Leaching sodium sulphate treated with sulphuric acid for yttrium 3 hrs S/L: 0.04 at 25°C

The yttrium released from the sample treated with sodium oxalate leached with sodium hydroxide was almost negligent (Fig. 5.8). Basically, the sodium hydroxide has no effect on the sample treated under mechanical treatment.

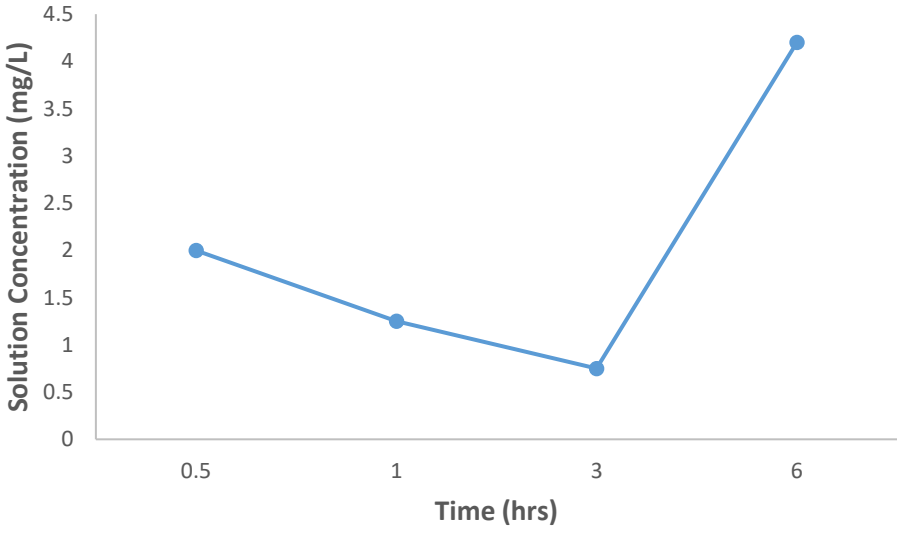

Figure 5.8: Leaching sodium oxalate sample treated with sodium hydroxide for yttrium 3 hrs S/L: 0.04 at 25°C

5.4 Conclusions

There are many studies showing that organic acids increase the dissolution of many minerals relevant to rare earths. These reagents have been shown to have varied influence based on several properties such as the number and position of hydroxyl/carboxyl groups, molecular structure and proton dissociation. In previous study, oxalic acid was able to enhance the dissolution of phosphorus in monazite concentrate. Monazite and xenotime are rare earth phosphates and had similar chemical composition. Whereas, in the case of xenotime, organic acids have shown almost negligible capability to solubilize the mineral. It seems that the covalent bonds are strong enough to avoid any chelate or ligand between them.

Furthermore, mechanochemical treatment has been used in several processes to improve the leaching process. Unfortunately, this does not increase leaching quantity in this study at all. The reagents used (sodium sulphate and sodium oxalate) were not able to transform the xenotime concentrate to a more amenable species to be leached.

To sum up, monazite has a monoclinic crystal structure so that may allow it to solubilize. Xenotime displays a tetragonal crystal structure which may avoid any kind of binding. Even increasing the temperature displayed no real effect on the solubilisation. Decreasing the pH did not display any effect at all either. Using mechanochemical treatment and increasing the milling time did not increase the solubilisation of REEs efficiently enough. There was no indication of potential reasons found in the literature why this process works for monazite but not for xenotime. Due to the secondary nature of this to the project, no further experiments were carried out to this end".

CHAPTER 6.
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The methods of processing REEs involve highly corrosive conditions, high temperatures and consume large proportions of reagents. The most common industrial process for monazite treatment involves an acid roasting process in which concentrates are combined with concentrated sulphuric acid at temperatures in excess of 200°C. In addition, due to the co-extraction of a large proportion of impurities and the chemical similarity of the REEs, separation and purification from such a process is extremely complex and expensive. There is a strong interest in developing a viable alternative of extracting rare earth elements employing more benign reagents and moderate conditions. This situation has led to the discovery of a potential new direct leach approach using low molecular weight organic acids.

The present study developed an alternative method of processing monazite concentrate at the laboratory scale, in which rare earth elements are extracted from the monazite concentrate in two leach stages and subsequently precipitated as a compound (RE hydroxide) in the final stage. This last compound may be used to feed the solvent extraction (SX) separation process. The most important advantages of this process involve non-aggressive reagents and not high temperatures.

The literature review unveiled that there is limited material relating to the use of organic acids for the extraction of rare earth elements. However, there were several sources displaying the ability of organic acids to selectively complex the rare earth elements, suggesting the potential for selectivity leaching

The available information regarding the use of organic acids to precipitate rare earth elements are widely known in conventional processes. Oxalic acid has been employed to precipitate REEs from the rare earth phosphate solution which show a hint that organic acids may be used to leach monazite concentrate

The developed method consists in three stages which are described below:

First stage: Oxalic acid achieved the dissolution of monazite concentrate, denoted by the solubilisation of phosphorus. During this stage, the phosphate mineral is dissolved and the REEs are reprecipitated as a solid oxalate compound. The conversion to REE oxalate is limited by the consumption of oxalic acid, which also binds with solution species. Interestingly at room temperature, this process is highly favoured over iron dissolution. Increasing the temperature in the solution, decreases the time required for conversion but increases the relative dissolution of iron and thus further limiting the conversion extent achieved. The conversion of REE oxalate is affected strongly by the pH, which must be ~1 for rapid dissolution. A critical point is the impact of water quality as an attempt to recycle plant tailing water with significant dissolve solids greatly impacted the extent of conversion.

The solid-liquid ratio is important in the conversion to RE oxalate due to the limitation of oxalic acid availability. Adding fresh oxalic acid or making a second pass aids to increase the extent of conversion to RE oxalate. The long term leaching (7 days) of oxalic acid shows that the solubilisation of phosphates started decreasing over time. When fresh oxalic acid was added to the concentrate, the release of phosphorus began again at approximately the initial rate (from time 0). This may be important in the industrial scale where several sequential tanks may be necessary to optimize at large scales, but also suggests that there is no significant passivation effect occurring. The RE solution concentration was negligible, therefore it

demonstrates the creation and re-precipitation of RE oxalate. The residue was characterized by XRD to confirm the formation of RE oxalate. The best results in this study were achieved under these conditions: 0.8M, pH 1, 500 rpm, S/L=0.1, 65°C and 10 hours.

Second stage: The addition of an alkaline EDTA solution resulted in a rapid release of REEs from the pre-treated monazite concentrate. Solution pH showed significant influence with increasing dissolution at more alkaline conditions. This agrees well with stability diagrams and literature suggests the formation of a mixed REE-oxalate-EDTA solution species. High recovery is achieved in atmospheric conditions (25°C). Further temperature elevation of the EDTA decreased the recovery of the REEs, potentially through accelerating other reactions. The recovery of rare earth elements is significant (high for Nd, almost 60%), more than 40% of Ce and La and low content of impurities (P and Fe) in the solution. Furthermore, the reaction is very quick (full extraction achieved in 5 minutes). This rapid reaction may be a great advantage at the industrial scale. The best results were under these conditions: 0.1 M, pH 10, 700 rpm, S/L=0.1, 25°C and 5 mins.

Third stage: The addition of NaOH to the EDTA leach solution at high temperature was able to precipitate a RE hydroxide. The creation of RE hydroxide is an important advantage to employ this process in industrial scale as it may feed conventional solvent extraction (SX) technology. RE hydroxide is the material currently used in conventional processing to feed the solvent extraction stage, therefore this process may be run without the need to amend the purification stages. The conditions tested were: 2.5 M, $L_{REE\ EDTA\ oxalate}/L_{NaOH}$=50mL/100mL, 95°C and 1 hour.

Xenotime (another rare earth phosphate) was also tested but achieved poor results although the minerals shares a similar chemical composition. Another approach has been tested (mechanochemical treatment), again resulting in vastly lower REE dissolution. It seems that the crystal structure may play an important role in the feasibility of processing monazite but not for xenotime.

The proposed flowsheet, which has three main stages described previously, works properly as an independent stage. Each stage needs to determine for the optimal conditions. The full flowsheet, which connect the different main stages, will require other technologies to maximise the recovery of REEs.

6.2 Recommendations for the future research

The timeframe of the present research and original approach to REEs from monazite concentrate have led several interesting points which needed to be investigated further. Some of them are:

- Determine the optimal conditions of the oxalation stage which may include several tanks and the influence of the having smaller particles from the monazite concentrate. It seems that the recovery of REEs can be improved significantly by adding fresh oxalic acid, optimal time and temperature.
- In industrial scale, achieving the optimal conditions in EDTA stage is a must. The quick reaction present in this stage is a boost in this novelty process. Improving the first stage (oxalate) should be reflected in high recovery in second stage. The effluent of the third stage (EDTA 4Na) can be used in the second stage and it is important to confirm and determine the ratio of mixing to get the highest recovery.
- The liquid/liquid ratio ($L_{RE\ EDTA\ oxalate}$ / $L_{\ NaOH}$) must be investigated in the third stage. The actual concentration (2.5 M) is vast high. Screening experiments conducted have shown that the liquid/liquid ratio can be dropped to 50/50 mL and 1 M NaOH. Therefore, it is a must to confirm the minimum concentration and liquid/liquid ratio. Furthermore, temperature and time may be investigated as well, therefore, they can be decreased and reduce producing cost.
- Perform further investigation with xenotime using organic acids. Although xenotime and monazite are rare earth phosphates, this novelty process in laboratory scale does not work at all for xenotime.

APPENDIX 1

SILICATE, PHOSPHATE AND CARBONATE MINERAL DISSOLUTION BEHAVIOUR IN THE PRESENCE OF ORGANIC ACIDS: A REVIEW

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1. Abstract

Researchers in the field of geoscience have identified several effects on the stability of the surrounding minerals caused by naturally occurring solution species. Organic acids and their conjugate salts have been shown to provide significant influence on a wide range of minerals, generally increasing elemental mobility and aiding in solubilizing the solid matrix. Their ability to complex elemental and molecular species, presents interesting opportunities in manipulating systems to achieve outcomes that are otherwise not thermodynamically favored. Such properties form the basis of some analytical techniques such as the toxicity characteristic leaching procedure (TCLP) used in environmental assessment of waste product stability and the acidified ammonium oxalate (AAO) process used to selectively dissolve poorly crystalline iron oxide phases.

These characteristics also present the opportunity for use of these species to aid in industrial dissolution of value-containing minerals (extractive metallurgy). Such an approach provides the basis for the current review. The literature has been reviewed to identify organic acids - particularly low molecular weight organic acids (LMWOAs) - that significantly aid dissolution of relevant minerals, trends in their behavior and fundamental explanations for these observations. It is also of interest to find evidence that these acids may improve selectivity in a hydrometallurgical application. This review is limited to silicate, carbonate and phosphate minerals as they represent the information relevant to the ongoing research.

Formic and acetic acids had the greatest impact on minerals composed of group I and II elements, while citric, oxalic, EDTA and salicylic acids represent the most promising options for transition metal and lanthanide-based minerals. The variation between the effect of the acids as well as a degree of the selective nature of their effect can be attributed to differences in the stability of the metal-ligand complex formed. pH plays a highly significant role, assisting the dissolution through, altering the dissociation of the acids, modifying the surface charge of the mineral, acid attack, maintaining the solubility of other dissolved ions and/or altering the mechanism involved. The crystal structure and secondary reactions occurring with other constituents in the mineral alter their amenability to dissolution in organic acids.

2. Introduction

Organic acids are common, naturally occurring compounds, distinguished by the presence of the carboxylate (COOH) functional group. These range from very simple molecules such as

formic acid (CHOOH) found in many ant species, through to DNA, the blueprint of complex life. LMWOA is a somewhat subjective term as the spectrum of molecule sizes is so great and each application may have a different perspective on what constitutes low molecular weight species. For the purpose of this paper the term includes aliphatic and aromatic compounds with 1-3 carboxylic acid functional groups.

2.1 Organic Acids in Geochemistry

The relationship between LMWOAs and mineral surfaces has been studied for several decades and is an important geochemical process (Wei, 2011). LMWOAs are commonly present in rhizosphere soils and distinctively found in the layer next to the soil-root interface (Kong, 2014). According to Lines-Kelly (2005), "the rhizosphere is the zone of soil surrounding a plant root where the biology and chemistry of the soil are influenced by the root". These acids are created mainly by the decomposition of plant root systems, fungi residues and other organic material (Wang, 2005). An example are the prokaryotes, which are the first land-colonizing organisms, which primarily create aliphatic acids and, to a lesser degree, aromatic compounds (Neaman, 2005). The structures of some common aliphatic and aromatic acids are given in Figures 1 and 2.

Organic acids such as fulvic and humic acids, which are present in geological weathering systems, break down minerals to create metallo-organic chelates (Huang & Keller, 1972). Furthermore, organic acids (such as oxalic and citric acid) play an important role in many processes in the rhizosphere, i. e. metal detoxification and mineral weathering . They have also shown an ability to influence geochemical processes such as concentration of elements, transportation and dissolution (Kiang, 1972).

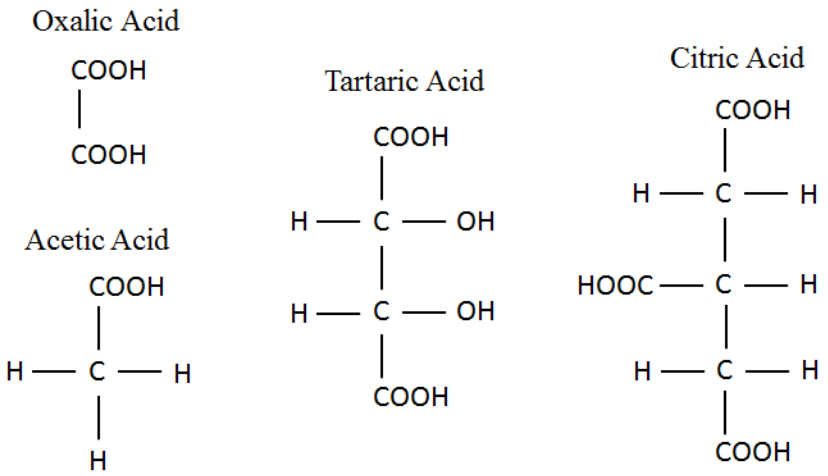

Figure 1: Chemical structure of some common aliphatic acids.

Mineral weathering may be increased by organic acids and their anions (conjugate bases) (Drever & Stillings, 1997; Wang et al., 2005). The presence of carbonyl and hydroxyl functional groups in the organic acids structure allow the creation of complexes with elements in the soil (Kong, 2014). Mineral weathering by organic acids can be explained by at least three factors: (a) changing the speciation of ions in solution; (b) influencing the solution saturation with respect to the mineral; and (c) perturbing the dissolution reaction far from equilibrium (Drever & Stillings, 1997).

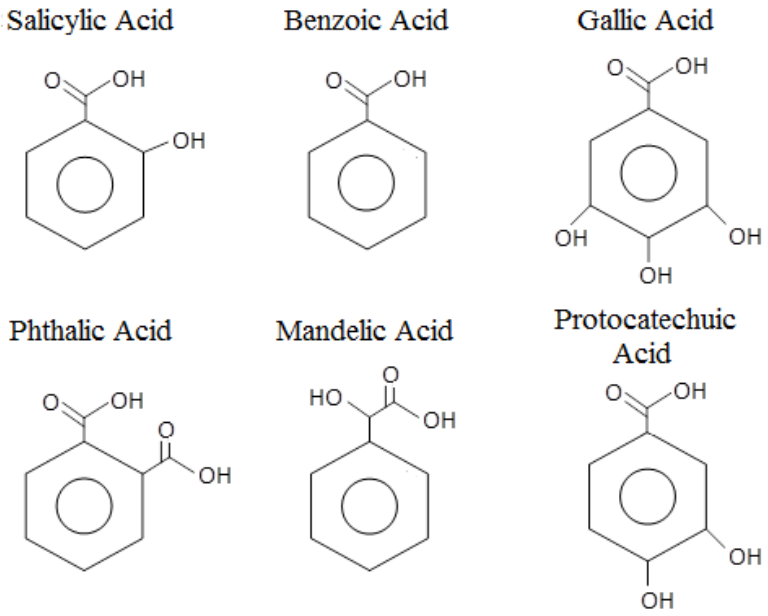

Figure 2: Chemical structure of some relevant aromatic acids.

2.2 Applications in Extractive Metallurgy

It has been established that organic acids and their conjugate bases can be of great value in the minerals industry. One of the United States Environmental Protection Agency's (EPA) key tests for assessing the stability of toxic elements in waste material (TCLP) (EPA, 1992) contains acetic acid as a buffering agent. This test is used to determine the ability of toxic components including arsenic, lead, mercury, etc. to be released upon storage of waste products in or near natural systems. Also the acidified ammonium oxalate (AAO) (Smith, 1994) procedure for selectively dissolving amorphous/nanocrystalline iron oxides and hydroxides is a useful characterisation technique.

There are also examples of research evaluating the potential of organic acids for direct employment in mineral processing applications. The well-established complexing properties of these species has inspired research into a multitude of applications. This carries on from a significant history of complexation reactions in the extraction stage of metallurgy including the use of cyanide in gold leaching, employed since the 1890's, and ammonia in nickel processing (Caron process), established in the 1950's.

Nickel laterites are oxide ores generally with low nickel contents dispersed throughout the gangue minerals, these are difficult to treat and represent up the 70% of know nickel reserves (Ntloyakhumo, 2008). The author used oxalic acid to leach iron selectively over nickel as a method of upgrading the ore and releasing trapped value. As they are not significantly upgraded via physical separation or flotation, a method of beneficiating nickel laterites ores before leaching, is highly important to improve the economics of the process. A similar study involved using citric and oxalic acids sequentially to selectively remove the various components of interest (Ni, Co and Fe) (Kursunoglu, 2015).

A range of other studies have investigated the use of organic acids in extraction, (Fischman, 2009) showed the value of using citrate as a complexing agent for iron in the ammoniacal leaching of awaruite (Ni_3Fe). Without citrate dissolved iron would reprecipitate as a hydroxide on the mineral surface forming a passive barrier to leaching. (Li, 2015) displayed that a high

proportion (>95 %) of lithium and cobalt could be leached from spent lithium ion batteries using a succinic acid leaching system. (Park, 2013) described the extraction of Pb, Cu and Zn from contaminated soils using citric acid. Gharabaghi et al. (2010) reviewed the potential of organic acids fir the beneficiation of calcareous phosphate ores.

3. The Effect of Organic Acids on Relevant Minerals

Organic acids induce multiple effects on various aspects of compounds and the reactions are governed by a variety of phenomena. Therefore a review of literature spanning the interactions of organic acids with as many varieties of relevant minerals as possible will provide the greatest insight on not only the effect of the species on dissolution but also the underlying reactions and factors that influence this behaviour. All mineral compositions for this section are provided in table A1 in the appendix.

3.1 Basalt

Basalt represents material composed of a range of minerals. The major phases present are silicates and aluminosilicates such as plagioclase, feldspar, alkali feldspar, quartz and augite.

The experiments carried out by Neaman et al. (2005) investigated the dissolution of basalt in the presence of organic acids. The impact of both aliphatic ligands (acetate, citrate, formate, fumarate, glutarate, lactate, malonate, oxalate and succinate) and aromatic ligands (benzoate, gallate, phthalate and salicylate) were examined under the following conditions: pH 6, 0.001 M ligand, 30 mg sample in 30 mL of solution, in both oxic and anoxic conditions over 28 day reaction times. The reagents that displayed the greatest rate of dissolution (citrate, oxalate, gallate and malonate) were investigated at higher concentration (0.01 M, 300 mg sample, 30ml solution) with all other conditions remaining constant.

The presence of organic ligands improved basalt dissolution in all cases with respect to blank tests in the absence of these reagents. The aliphatic acids displayed a significantly greater ability to release the elements of interest (Fe, Al, Mg, Si and P) than aromatic acids, this was attributed to protonation of the functional groups of the aromatic compounds. It also appears that the relative effect of each reagent correlates well with their respective complex stability constants, and the greatest influence was observed in species with the greatest number of binding sites (tri- and tetradentate ligands). There was a slight decrease in the dissolution observed at higher ligand concentration, suggesting a limit to the influence of these species and possible solubility effects. Interestingly, anoxic conditions appeared to inhibit dissolution at the lower organic concentration (0.01 M) but then improve it at the elevated levels (0.1 M).

3.2 Feldspars

Feldspars, composed by calcic plagioclase, albite and microcline, were investigated under the effects of oxalic, citric, salicylic, protocatechuic, gallic, p-hydroxybenzoic, vanillic and caffeic acids by Manley (1986). Mineral samples were placed in 15 mL of solution at a solid/liquid ratio 1:1 (v/v).

The order of impact on element release was observed to be citric ~ oxalic > salicylic >> protocatechuic ~ gallic > p-hydroxybenzoic > vanillic ~ caffeic. Citric acid induced the greatest release of Si, Al, Ca and Na from calcic plagioclase. It has been suggested that under leaching conditions of feldspar in laboratory conditions, the strength (first ionization constant) of LMWOAs is likely more important in the release of elements from minerals than the ability of the acid to complex minerals. The amount of mineral dissolution (weathering) was calcic plagioclase > microcline > albite and was independent of the acid used. The author did not

explain why some minerals responded better that others, however it is likely due to the impact of the crystal structure.

Kiang (1972) examined the dissolution of oligoclase, albite, bytownite, anorthite, labradorite and high K plagioclase (andesine) at room temperature in the presence of aspartic, salicylic, acetic and citric acids. Three grams of each sample was poured into 250 ml of 0.01 M organic acid solutions and shaken continuously for 1, 6, 12 and 24 days.

In terms of dissolution, the order of decreasing effectiveness was citric, salicylic, aspartic and acetic acids. Citric acid has shown the highest efficiency in extracting Ca and Al, especially from Ca-rich plagioclase, apparently due to the creation of Al- and Ca- complexes. The dissolution of anorthite, labradorite and albite, displayed a strong complexation with salicylic acid but weak complexation with aspartic acid.

Welch (1996) investigated bytownite, two labradorite samples, albite and quartz in a mixed-bed flow-through reactor in acidic aqueous solution in the presence of oxalic acid and catechol. The dissolution rate is affected by the nature of the ligand. Oxalate has a strong impact in the dissolution rates of the Ca- and Al-rich members. Also, Catechol creates complexes with Al and Si and accelerates dissolution rates. Dissolution rates followed the sequence observed by Goldich (1938): Ca, Al rich feldspars weather more rapidly than Na, Si rich feldspars.

3.3 Fluoride Minerals

The release of F is an important process achieved using the influence organic acids. Tang (2013) investigated how secretion of organic acids (malic and citric acids) from roots influences F availability in soil. 5 g of soil and 40 ml of 5 mM citric or malic acid solution (pH 5.5) were added to plastic centrifuge tubes (50 ml). These tubes were agitated for 0.5, 1.0, 3.67, 10.28, 20.42, 60.02, 140.22 and 280.09 hours at a speed of 120 strokes per min. Malic and citric acids enhance to release F from rhizosphere soil.

Both the citric and malic acid extractions indicated a rapid release of F at the beginning, which may be the exchange of organic acid ion with surface F in the soil. This is followed by a decrease in the rate, which might be a second mechanism involving the interaction of organic acids with clay minerals and created compounds with metals cations, resulting in the F release. Several variables affect the level of F ion release such as soil surface charge, complex stability constants, pH, and the position and number of functional groups in the organic molecule.

It has been noted that the surface charge of colloidal soil particles may greatly impact several of its properties Yu (1997). Adsorption of various ions has been shown to impart significant influence on the surface charge of said particles, in turn altering their behavior. Zhao (2006) studied the affinity for fluoride adsorption and desorption on two variable charge soils in the presence of LMWOAs (citric, malic, malonic and oxalic acids). 1.2 g of soil sample, 30 ml of the solution containing 0.01 mol L^{-1} KCl and organic acids of various concentrations (0.5, 1.0, 2.0 3.0 mmol L^{-1}) were added in centrifuge tubes, shaken for 3 h in a water bath at 25°C,then let stand for 21 h and finally centrifuged for 10 min at 3000 rpm. Oxalic and malonic acids have shown stronger influence than citric and malic acid, said to be due to simpler chemical structures. Organic acids were shown to be more effective in fluoride adsorption at high pH.

3.4 Silicate Minerals

Huang (1972) examined the behaviour of several silicate minerals such as augite, muscovite, labradorite, microcline, kaolinite, illite, a refractory clay and montmorillonite in the presence of acetic, aspartic, citric, tartaric, salicylic and tannic acids. Minerals decomposed more readily in organic acids (through the solubilisation of framework cations) than in pure water.

Basically, in the case of silicate minerals, dissolution rate is based on the complexing property of the organic acids.

Barman et al. (1992) studied the influence of citric, oxalic, glycine and salicylic acids on several silicate minerals such as olivine, epidote, tourmaline, hornblende, biotite and microcline. 0.5 g of each mineral was added 25 ml of 0.5 M oxalic acid (pH 0.5), 0.5 M citric acid (pH 1.0), 0.01 M salicylic acid (pH 2.3) and 0.5 M glycine (pH 5.6) into plastic bottles. The bottles were agitated on a horizontal shaker at 27 °C for 5 hours each day and allowed to reach equilibrium for the remaining 19 hours. The solutions were filtered after 24, 48, 72, 96 or 120 hours and analyzed.

The nature of the acid influences the relative stabilities of the silicate minerals. Solubilisation seems to be influenced by three factors; (a) structure of the mineral, (b) composition of the mineral and (c) nature of the acid. The results indicated that the organic acids decomposed silicate minerals via simultaneous actions of acid attack and chelation. The order of solubilisation in the presence of organic acids suggests that the position of the cations in the crystal is a determinant variable in the order of solubility of silicate minerals. The most soluble species are epidote and hornblende due to the presence of ions (Ca^{+2}) in interchain spaces

3.4.1 Clay Minerals

There are several studies related with clay minerals. A summary of the most relevant findings are described in Table 1. Generally the presence of organic acids increase both the rate of dissolution and the overall solubility of clay minerals. There was also distinct variations in the degree of the effect, which correlates with binding energies of the various acid species with the relevant cations.

3.5 Magnesite Ores

Formic acid was investigated for leaching natural magnesite ores by Raza et al (2014). 5g of mineral sample was combined with 500 mL of 8% formic acid and agitated at 350 rpm with variations in temperature from 45 to 75 °C. Formic acid proved to significantly enhance magnesite leaching and the optimum concentration found to be 8% with a liquid/solid ratio of 14:1 mL/g. Raising the temperature caused an increase in the reaction rate.

Table 1: Summary of relevant conclusions of the interaction of clay minerals and organic acids.

Author	Samples	Outcome	Findings
(Huang, 1971)	Montmorillonite Illite Kaolinite	After a high rate of dissolution over 24 hours, the rate declined. Complexes of Al and Fe were likely formed increasing leach rates.	Cations in the clay minerals (Si, Al, Mg and Fe) are more soluble in complexing organic acids than in pure water.
(Kong, 2014)	Montmorillonite Illite Kaolinite	Oxalic acid displayed a stronger release of Si from all three minerals than citric acid under the same parameters.	Organic acids and their anions (conjugate bases) promote weathering in clay minerals Acids have different affinities for various elements.
(Wang, 2005)	Kaolinite	The effectiveness of anionic ligands to increase kaolinite dissolution, arranged in decreasing order was oxalate>citrate>malate.	The rate of dissolution was influenced by the concentration of organic acid and the degree of protonation of the ligand (i.e. L2-oxalic; HL-oxalic; H2Loxalic).
(Cama, 2006)	Kaolinite	The dissolution rates in the presence of oxalate were up to 30 times faster than at the same pH and temperature in its absence.	The formation of Al-oxalates (AlOx, AlOx2 and AlOx3) strongly attenuate the activity of free aluminium (Al^{+3}).

3.6 Phosphate Minerals

3.6.1 Dicalcium and Tricalcium Phosphates

Experiments conducted by Johnston (1952) have shown the ability of a wide range of organic acids to decompose dicalcium and tricalcium phosphates. This property had not previously been reported. The results indicated that the reaction is not only dependent on the pH of the solution but also it is closely affected by the structural composition of the acid. Hydrogen ions are necessary to aid the reaction, however they are not the most important variable which affects the solubility. It appears that the most important variable is the structure of the organic acids.

Johnston (1954a) further work confirmed that aliphatic acids were capable of attacking tricalcium phosphates predominantly based on the structure of the acid. Oxalic, pyruvic and tartaric (aliphatic) acids demonstrated a large influence. Gluconic and galacturonic (sugar) acids are also able to dissolve the minerals at a high rate. Two different sets of experiments were carried out: 1) Shaken tests: 1g of tricalcium phosphate and 30 mL of N/10 acid solution were mixed and shaken for 48 hours at 20°C. 2) Static tests: 5 g of tricalcium phosphate, 30 g of quartz sand and 150 mL aliquots of the acid solution were placed in a non-agitated flask. Both methods achieved very similar recoveries, suggesting that agitation has little impact.

The presence of more hydroxyl groups per molecule is important to release P_2O_5 and it can be observed from the data in Table 2. The addition of one hydroxyl group (OH) from acetic to glycolic acid increased the release of phosphorus rate. Also, the addition of one phenyl group (benzene ring) from glycolic to mandelic produced the same effect as well.

Table 2: Release of P_2O_5 under the effects of different organic acids (Johnston, 1954a).

Acid used	[P_2O_5] (mg/100mL)
Acetic	129
Glycolic	249
Mandelic	284

A similar effect was observed in other acids along with the influence of the molecular structure (Table 3). The addition of two hydroxyl group (OH) from butyric to α-hydroxyisobutyric acid and from butyric to β-hydroxybutyric increased the release of phosphorus rate. On the other hand, keeping the numbers of hydroxyl group in α-hydroxyisobutyric and β-hydroxybutyric shown a decrease in the release of phosphates due the different number of carbons and its configuration.

Table 3: Release of P_2O_5 under the effects of different organic acids (Johnston, 1954a).

Acid	[P_2O_5] (mg/100mL)
Butyric	123
α-hydroxyisobutyric	228
β-hydroxybutyric	155

Johnston and Miller (1959) conducted further experiments with aliphatic acids and calcium phosphate. The degree of dissolution is governed by (a) the capability of the acid anion to create stable solution species or to generate precipitated compounds with calcium, (b) the strength of the organic acid and (c) its dissociation constant. The acid strength and the stability of metal-organic complexes are influenced by the structure of the acid.

The presence of the second carboxyl group has a strong effect on the reaction and this second carboxyl group (generally only slightly dissociated) decreases the acid strength and an important reduction in the amount of phosphate that dissolves into solution. This effect aids in the removal of calcium ions from the reaction by association. Therefore, the reaction can go much further and raises the presence of phosphate into solution.

Johnston (1954b) enhanced his previous findings by conducting experiments with aromatic acids. 3 g of tricalcium phosphate was added to 90 mL of N/10 acid solution. The mixture was shaken for 48 hours at 20°C and then filtered. The results (Table 4) indicate that several aromatic acids also possess the ability to dissolve tricalcium phosphate. The reaction is again mainly affected by the structure of the acid.

Table 4: Phosphate release by aromatic acids from tricalcium phosphate (Johnston, 1954b).

Acid	[P_2O_5] (mg/100mL)
Salicylic	254
2,4 dihydroxybenzoic	242
Mandelic	284
Acetylsalicylic	221

There are several interesting points to note from these experiments (Table 5). The first is that the influence of the acid on dissolution doesn't seem to be related to its solubility (unless the desired lixiviant concentration is above its saturation level). As mentioned previously, the dissociation constant of the various acids play an important role. Another point of interest is that the capacity of benzoic acid to dissolve phosphate is greatly diminished by the replacement of an amino group into the benzene ring.

Table 5: Values of P removed, dissociation constant and solubility (Johnston, 1954b).

Acid	P_2O_5 removed	Dissociation constant	Solubility of acid
Benzoic	127 mg	6.5×10^{-5}	0.27 g/100 ml H_2O
Mandelic	284 mg	4.3×10^{-4}	16 g/100 ml H_2O
Salicylic	254 mg	1.06×10^{-3}	0.18g/100 ml H_2O

3.6.2 Iron and Aluminum Phosphates

Johnston (1959b) performed further experiments using organic acids and aluminum and ferric phosphates (Table 6). Again, the structure of the acid (likely number and position of functional groups) affects the interaction with these insoluble phosphates. It is notable that hydroxy derivatives are more active in dissolving ferric phosphate than their unsubstituted parent acids i.e. lactic and propionic acids. There is not a clear trend in the order of effectiveness after citric in dissolving aluminum phosphates. However, if oxalic acid is eliminated, the trend is similar to that observed in ferric phosphates.

Xu et al., (2004) studied iron phosphate dissolution in the presence of acetic, lactic, malonic, malic, tartaric, oxalic, citric, ρ-hydrobenzoic and salicylic acids. Similar to the findings of Johnston, citric acid displayed the highest rate of P dissolution from iron phosphate having almost twice rate produced with oxalic acid.

Table 6: Phosphate released by organic acids from ferric and aluminium phosphates (Johnston, 1959b).

	$[P_2O_5]$ mg/100mL	
Acid	$FePO_4$	$AlPO_4$
Citric	440	300
Oxalic	200	114
Tartaric	165	67
Malic	165	173
Lactic	50	110
Propionic	17	Negligible

3.6.3 Calcium Carbonate Phosphates

There are several studies related with calcium carbonate phosphate minerals. Table 7 describes several important findings in this field. Interestingly, the major outcome was that many reagents selectively dissolved the carbonate material, leaving the phosphate relatively intact. As can be seen there have been some contradiction in the findings of various research efforts, which may point to variations in ore behaviour based on composition and structure.

Table 7: Findings from several studies on the effect of organic acids on calcium carbonate-phosphate minerals

Author	Samples	Outcome	Findings
(Sadeddin, 1990)	Jordan calcareous phosphate rocks.	Acetic acid enhances dissolution of calcium carbonate.	Gangue minerals have a strong effect in decreasing the carbonate content in the phosphate rock. Acetic acid solution leaches the calcium carbonate without decomposing the phosphate itself.
(Gharabaghi, 2009)	Low-grade calcareous phosphate.	The leaching rate of carbonate is improved by increasing the acid concentration, reaction, temperature, time and decreasing pulp density.	The dissolution rate of carbonate is a chemically controlled and occurs at the surface of the particle. Acetic acid solution does not attack the phosphate minerals. Stirring speed had not shown any effect on the carbonate dissolution rate.
(Economou, 1997)	Greek calcareous phosphates.	Acetic acid reacts mainly with calcite meanwhile almost all of the francolite remained in the solid phase.	Mechanical stirring has an important effect on the dissolution process. The temperature and concentration of acetic acid did not play an important role in the dissolution process.
(Gharabaghi, 2010)	Calcareous phosphates ores.	Formic and acetic acids have the tendency to attack the phosphate minerals (poor selectivity for carbonate) and can corrode equipment. Less corrosive effects and risk of phosphate mineral dissolution were achieved by lactic acid.	Leaching is less effective at high organic concentrations due to the polarity of the O-H bond. High temperature may increase the leaching efficiency but the temperatures may be limited due to low boiling temperatures and the decomposition of organic acids.
(Taghipour, 2013)	Calcareous soils of Western Iran.	Oxalic>citric>malic are the most effective acids which aid P release. Oxalic acid has a strong affinity for chelating metal ions avoiding their precipitation as phosphate species.	The ability of the oxalic acid to release P can be related to the formation of a soluble oxalate-metal-P complex. Precipitation of P ions can occur due to the capacity to chelate metals and the relatively strong acidity of its solution.
(Zafar, 2006)	Calcareous phosphate rock.	Optimisation of operating conditions: Temperature, 50°C; time, 35 mins; liquid-solid 5:1; acid concentration 6% and magnetic stirrer, 250 rpm.	Formic acid is used in industrial scale Demonstrated the ability of organic acids for leaching compounds.
(Zafar, 2007)	Calcareous phosphate rock.	Lactic acid dissolve carbonate material in low grade phosphate rock, therefore, it improved the P_2O_5 content.	The large polarity of O-H bond present in strong organic acids, may not react with pure calcium carbonate. However, in dilute solutions, organic acids react in selective leaching of carbonate.
(Ashraf, 2005)	Calcareous phosphate rock.	Succinic acid can be used to enhance of calcareous material in low-grade phosphate rock.	Succinic acid is not an adequate leaching agent below 37°C because of its limited solubility.

3.6.4 Phosphate Rocks (PRs)

There are several studies related with phosphate rocks (distinct from the calcareous phosphate rocks discussed above), the major findings of which are shown in table 8. Based on his observations, Pohlman (1986) stated that several variables played an important role in the rate of dissolution of soils in PRs. These are (i) rate of diffusion of organics from bulk solution and diffusion of products from the site of reactivity, (ii) contact time between mineral surface and organic acids, (iii) degree of dissociation of organic acids, (iv) position and type of functional groups, (v) chemical affinities of chelating agents for the metals.

Table 8: Finding in several studies performed in Phosphate Rocks

Author	Samples	Outcome	Findings
(Bolan, 1994)	Patua silt loam (volcanic ash) soil. Tokomaru clay loam soil.	In the case of monocalcium phosphate (Patua silt loam) Citric achieved 83.78% dissolved phosphate. Lactic achieved 8.71% dissolved phosphate.	The number and position of carboxyl (-COOH) and hydroxyl (-OH) functional group government the complex formation. The performance of organic acids to release P from PRs basically depends on the chelation of calcium and the supply of protons.
(Kpomblekou, 1994)	Kodjari, low reactive PRs North Florida, medium reactive PRs.	Oxalic and citric acids appeared to be the most efficient acid in releasing P.	The dominant factor, which determines the degree of release of P, seemed to be the type of functional groups and position within each carboxylic group. The hydroxyl group seemed to play an active role in the P release.
(Xu, 2004)	North Carolina PR (P content about 15.7%).	Citric acid displayed the greatest ability to dissolve P from PRs followed by oxalic and tartaric acids.	It appears that the presence of more carboxyl groups in the organic acid, the higher rate of P dissolve. The solubilization of P is enhanced greatly by increasing the concentration of organic acids except in the case of oxalic acid. It seems that when the concentration of oxalic acid is increased, the precipitation of calcium oxalate would inhibit further solubilization.
(Sagoe, 1998)	Phosphate rocks from China, Jordan, Togo, USA (Florida), Sri Lanka and Tanzania	Sulphuric and tartaric acids dissolved the same amount of P from PRs despite a tenfold difference in the free acid concentration.	Protonation reactions initially influenced the PRs dissolution which only explains 13-38% of the amount of P released. Therefore, most of the P release could be explained by other factors (ie. Chelation).

3.6.5 Rare Earth Phosphates

Organic acids have shown the ability to solubilize monazite and xenotime minerals. After long exposure times, humic acids considerably enhanced the solubility of monazite, which is opposite to the general opinion on the stability of phosphate compounds based on experiments conducted in nitric acid. The detected enhancement in the concentration of released elements and the monazite solubility demonstrates these species to be a potential alternative to conventional processing techniques (Polyakov, 2009). They may also aid in separation as the properties of neighbouring elements become more differentiable where the trivalent rare earth ions create compounds with organic molecules (Spedding, 1978).

Several organic ligands have shown an effective solution association with rare earth ions. However, the most extensive research has been conducted with aminocarboxylic acids (EDTA, HEEDTA, DCTA, DTPA, EGTA and EEDTA acids), where with the exception of Nitrilotriacetic acid, all of these ligands create 1:1 complexes with REEs (Topp, 1965).

Goyne (2006) studied apatite under the effects of organic acids. Dissolutions experiments were performed under anoxic and oxic conditions using centrifuge tubes as batch reactors. 0.3 g of each mineral was added to 30 mL of 0, 1, 5 and 10 mM acid solutions at pH 5. The acids were shown to release Ca and P, and phthalate, oxalate and particularly citrate displayed a strong release of yttrium from apatite. The release of Yttrium from apatite was not affected by the presence of O_2.

Similar experiments were conducted on monazite as well as apatite by Goyne (2010) using both aliphatic and aromatic acids. The results indicated that LMWOAs (citrate, oxalate and phthalate) aid to release rare earth elements and yttrium from monazite and apatite. Aliphatic acids proved to be more effective than aromatic species in achieving dissolution. Moreover, the absence/presence of dissolved O_2 (g) did not indicate any influence on REE release from phosphate minerals.

4. Implications of the acid/mineral interactions

The most obvious conclusion from the literature available was the general trend that organic acids aid in mineral dissolution. This is not outwardly revolutionary based on their ability to complex cationic solution species and thus decrease their activity, increasing the overall concentration achievable based on solubility. However, the breadth of this review highlights several additional facets of the interaction of organic acids and mineral surfaces. The variation in behaviour between different acids and minerals, the impact of conditions, the mechanism of dissolution and whether the process represents a legitimate potential process.

The variation in the impact of the acids can generally be attributed to the complexing behaviour of the ligand to the relevant cations in the mineral. As an example the increasing dissolution of calcium phosphate minerals from acetic to mandelic acids as the calcium complexes have K_1 values of ~1.6 and ~3.6 respectively (Sillen, 1971). The acid displaying the greatest impact on a particular mineral will vary based on the primary cationic components. Formic acid favour alkali metals, while many larger molecules favour transition metals. Preferential complexation of specific cations is the predominant factor behind selectivity, a characteristic that may be exploited in a leaching process. This suggests that a potential limitation on the use of organic acids as leaching agents is the stability of the complex formed relative to both its own solubility (such as nickel oxalate) and that of the mineral. Simply increasing mobility/solubility is far from achieving full extraction.

The anion likely plays an important role as its behaviour in solution may also limit the extent to which a mineral may be dissolved. Solubility being a significant factor, silicates for example being poorly soluble in most leaching systems. Subsequent reactions may produce relatively large impacts on the extent of reactions achievable. The reprecipitation of dissolved anions could passivate the surface, phosphate forms many insoluble salts and may redeposit on the surface. This may occur with other cationic components as is a consistent problem with iron in weakly acidic or alkaline leaching systems.

In their use of phthalic acid to dissolve forsteritic glass, (Morris, 2008) found that the acid bound to the magnesium and released it from the glass. The silicate groups surrounding the removed atom then polymerised to leave a magnesium-deficient surface. If a similar process occurred in silicate minerals, only near-surface cations would be available for extraction and extremely fine particles would be required for a viable recovery process. (Barman, 1992) describes the variation of different minerals behaviour due to the relative position of the elements in the crystal structure and thus how available they are to removal and what impact that will have on the surrounding atoms.

The mechanism of the dissolution in these systems is likely to be complex. While simply decreasing the solution activity of the elements thus promoting further dissolution is one method by which complexation aids dissolution, it is unlikely to be the main driver for vast improvements in leachability. The binding of complexing ligands to sites on the mineral surface and thus destabilisation of the compound around that site is likely a prominent factor. Gharabaghi et al. (2010) discusses that multiple studies describe calcium carbonate dissolution from calcareous phosphate ore by organic acids as a chemically controlled process. Morris and

Wogelius (2008) showed that control of the magnesium removal from forsteritic glass changes from chemical control to transport control during the process. Holmen and Casey (1996) discuss a change in the mechanism of reaction based on pH in hydroxamate-assisted dissolution of goethite. Below pH 4 the reaction involves reduction of the ferric ions, while above pH 4 a ligand-induced reaction (proposed to be replacement of oxygen with water at the detachment sites) occurs.

What is apparent from both the geochemical processes and uses of organic acids in assisting metallurgical processes is that they are significantly dependent on the conditions, particularly pH. There are several manners in which pH will impact the system; the first being the degree of protonation. The binding energy of the complex with a specific cation will differ somewhat based on whether the acid groups have the protons attached. However, where high proportions of dissolution are reported at one pH, a significant change at another is unlikely to be solely related to the degree of dissociation of the acid. Another factor would be adsorption of the acid on the mineral surface. The surface charge will change significantly with pH and therefore may interfere with the adsorption process.

Where the conditions may have the greatest impact is in systems that have multiple reactions occurring. This is likely to occur in higher systems with higher acidity and concentration. This may occur where (i) acid attack is significant in the leaching mechanism (Barman, 1992), (ii) reducing conditions alter the reaction mechanism (Holmen, 1996) or (iii) lower pH is maintaining the solubility of other constituents in the source material (iron, phosphate, etc.). Thereby pH is likely to be a highly important factor in the implementation of organic acids as leaching agents.

4.1 Industrial application

In terms of representing legitimate options for extractive metallurgical processes, the mineral interactions suggest significant potential in certain systems. The major considerations would then surround two points of focus; the material being treated and the conditions of the treatment system. Potential benefits would include the use of relatively benign reagents, likely at lower acidity/alkalinity than otherwise required, greater selectivity in both mineral dissolution and elemental control (as is the case with most complexing media), and potentially recyclable reagents. However, both technical and economic challenges would need to be overcome such as the solubility of the acids (many are relatively low in comparison to inorganic reagents), the expense of the reagents, reaction rates and extents and conditions required. It is likely that processes arising using these reagents will be highly specialised and will either not be applicable to other related materials or will need to be modified.

5. Summary

The data presented in the literature displays that, in most cases, the presence of organic acids increases the degree and/or rate of dissolution of silicate, carbonate and phosphate minerals. Based on the fact that the majority of these studies were conducted under fairly benign conditions, low acidity/alkalinity, low concentration, ambient temperature and pressure, etc., it is reasonable to assume that any effect observed should be accentuated in more aggressive conditions. This may present opportunities for their use in mineral dissolution in an industrial context, whether that be as the primary lixiviant or to facilitate another leaching system.

It is apparent that there is a significant variation in the influence across the range of organic acids. It was observed that, in general, the aliphatic acids were more effective at releasing greater proportions of elements than the aromatic acids. This may be due to several factors, the structure may limit the density of adsorption of the acid on the mineral surface, the binding energies of the complexes formed may be generally lower, the mobility of the acids and/or

complexes may be slower and thus diffusion effects are greater. It was also observed that among the acids, increases in hydroxyl functional groups improved elemental release along with shorter carbon chain length. Both of these relate to increased charge density in acids and may also be linked to more preferred conformations in complexing relevant ions. The more hydroxyl groups also increases the dissociable protons, increasing the possible acidity (still dependent on dissociation constants).

Finally, selectivity was raised as a significant observation. As in an industrial context, the elements require separation subsequent to leaching, any selectivity that can be enacted by the leach system itself decreases the requirement for further processing downstream. This may suggest that depending on the acids' ability to extract materials of interest, and the conditions required, these systems could provide flowsheet benefits over conventional processing techniques on top of environmental, operational cost and handling advantages.

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APPENDIX 2

Solubilisation of Monazite in Organic Acids

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Keywords: Hydrometallurgy, rare earth minerals, monazite.

1 Abstract

In the present study, the feasibility to employ organic acids in a hydrometallurgical process to extract rare earths elements (REEs) from monazite-bearing ore was studied. Conventional processing utilises aggressive reagents and high temperature and pressure to form minerals that are amenable to leaching. While the reagents are relatively cheap, large quantities are required and fully consumed in the reactions, leading to high energy, reagent and maintenance costs. The processes also have high associated health, safety and environmental concerns. Therefore there is a significant drive to identify alternatives to address these issues.

The approach was based on previous studies performed in the geochemical area, showing that several acids, such as oxalic, citric and phthalic, aid in the release of REEs from monazite and apatite. To predict the REE leaching capacity of the organic acids, monazite was studied in varying conditions, pH, concentration, solid/liquid ratio, and residence time at room temperature. Oxalic acid has shown a strong ability to enhance the solubilisation of phosphorus and transition of rare earths to an oxalate species.

In an industrial context, the release of phosphorus in the solution, creation of rare earth oxalates and subsequent ability to form a rare earth hydroxide are highly important in viably processing REEs. The evidence may also suggest some selectivity in the process, leading to the possibility of decreasing the complexity of individual separation of the various REEs. The data presents the potential of this approach to provide an alternative conversion and leaching process that represents potential gains in cost, environmental impact, health and safety.

2 Introduction

The rare earth elements (REEs) are the group of elements predominantly composed of the lanthanide series from 57 (lanthanum) to 71 (lutetium) inclusive. These elements have similar properties to yttrium and scandium, therefore, they are included in the rare earth series (Kremers, 1961). The rare earth elements may be grouped in light rare earths from lanthanum to europium and heavy rare earths from gadolinium to lutetium (Balachandran, 2014) In another classification, the light rare earths (from lanthanum to samarium) are called the cerium subgroup, the middle rare earths (from europium to dysprosium) are called the terbium subgroup, and the heavy rare earths from (holmium to lutetium and yttrium) are called the yttrium subgroup (Kremers, 1961). Even though yttrium and scandium are not REEs, they are attached to the group because they are the precursors of the rare earths (Topp, 1965). Scandium posseses different properties to yttrium and the lanthanides, thus, it is not categorized in either subgroup (Topp, 1965).

REEs possess unique propeties which make them very valuable in industry. The list of goods that contain REEs is almost interminable. New magnets (which contain REEs) are more powerful and much lighter. Hence, many electronic products are becoming smaller. Military equipment such as cruise missiles, night- vision goggles, etc need REEs in their electronic

circuits, etc (Folger, 2011). China began REE production in 1980 and has become the predominant producer since the mid-1990s. Western producers have to face great competitiveness from Chinese REE companies due to government support, lenient environmental regulations and inexpensive labour and materials (Folger, 2011). The first Chinese REEs'export quota was set in the early 2000s, then it was seriously reduced in 2010 and 2011 (Simandl, 2014). China is both the top consumer of the REEs and producer (almost 90%) (Frik, 2015). China axed its export quota in January 2015 (Yap, 2015) but there is some uncertainty as to the duration that this policy will remain (Frik, 2015). Some countries, in particular Russia, Australia and USA, are pushing the development of new rare earth deposits in efforts to gain a more significant market share.

Aside from scandium, these elements do not occur naturally as their individual, native elements but are found as mixtures in different percentages (Spedding, 1978). Monazite, xenotime, allanite, gadolinite and bastnasite are the most common of these rare earth minerals (Panda et al., 2013). In an industrial scale, monazite, xenotime and bastnasite are the only minerals that have been exploited (Jordens et al., 2013). Current processing techniques are a variety of methods that either convert the rare earth minerals to more easily solubilized phases or effectively digest the feed. Inorganic acids, electrolytes, chlorine gas and alkalis are the predominant reagents (Zhang & Edwards, 2013). High concentrations of H_2SO_4 (98%) or NaOH (70%), high temperatures (from 150 to 600 °C) and pressures are needed to process monazite and xenotime (Franken, 1998). These techniques thus have high energy requirements, require corrosion resistant materials, have significant associated maintenance, potential hazards and generate highly hazardous by-products (vapours and tailings).

There has been limited research on RE leaching using non-aggressive reagents or research has not been published. There has been several attempts to use less aggressive reagents such as ammonium sulphate (Moldoveanu & Papangelakis, 2013), ammonium chloride (Chi et al., 2004) and hydrochloric acid-aluminum chloride (Li et al., 2013) but as yet none have shown potential as viable alternatives.

Geochemical processes have reported promising outcomes on the extraction of REEs that might be effective in mineral processing. Several studies conducted in the geochemical area (Bolan et al., 1994; Xu et al., 2004; Goyne et al., 2010) have suggested that the low-molecular-weight organic acids (LMWOAs) may have a significant effect in REE processing. Mineral dissolution was enhanced under the effect of oxalic, citric and phthalic acids and increased the release of REEs and yttrium from monazite and apatite minerals (Goyne et al., 2010). This paper discusses the preliminary success of using an alternative system comprised of more benign reagents under atmospheric conditions.

3 Materials and methods

The material tested in this investigation is a monazite concentrate donated by an industry partner. The concentrations of the main components of interest are given in Table 1:

Table 1: Assay of monazite concentrate

Element	Grade (wt%)
Ce	14.36
La	8.65
Fe	16.25
P	7.24

A Mastersizer 3000 using a Hydro EV analyser was used to perform the particle size distribution analysis. The P_{80} of the material was determined to be 87 µm. Powder X-Ray diffraction analysis (XRD) was performed by an Olympus BTX-II diffractometer to obtain structural information.

Monazite concentrate dissolution was tested under the effect of tartaric (AR), citric (AR), oxalic (AR) and maleic (LR) acids. Previous study performed by this team selected these organic acids as the most promising reagent options. Additional experiments were performed using tailings water from the same site where the major impurity components are described in Table 2.

Table 2: Analysis of tailings water

Element	Units	Quantity
pH in water	pH units	7.9
Total dissolved solids (grav)	mg/L	3100
Total suspended solids	mg/L	20
Sodium dissolved	mg/L	1100
Bicarbonate HCO_3 as $CaCO_3$	mg/L	320
Chloride in water	mg/L	1100
Sulphate in water	mg/L	690
Hardness as CaCO3	mg/L	290
Silica dissolved	mg/L	120

Screening experiments were studied to confirm the trend of the varied response of different organic acids observed in previous work. 250 mL Erlenmeyer stoppered flasks were used to perform the experiments. The pH (2 and 5) and type of organic acid were the main parameters studied with temperature, leach time, molar concentration and solid/liquid ratio all being constant.

10 g of monazite concentrate was combined with 100 mL of solution of each organic acid under the relevant conditions. Sulphuric acid and sodium hydroxide were utilized for pH adjustment. Once thoroughly combined, the 8 flasks were placed in a Labwit ZWY-211B incubator shaker at 100 RPM for 24 h at ambient temperature (25 °C). The 8 solutions were filtered and the solids washed with deionized water. The ICP-OES (Agilent 5100 Synchronous Vertical View SVDV) performed the analysis of the solutions.

Oxalic acid, the acid showing the most potential dissolution, was chosen for further study. A 1 L Duran flat range reaction vessel agitated by a Heidolph Model RZR-1 overhead stirrer was chosen to conduct larger scale tests. The influence of additional parameters (further pH change, residence time and tailings mine site water) were studied and solution samples (10 mL) were taken to observe the reaction over time.

Three experiments of duration 24 h, 168 h and 72 h were carried out. The oxalic acid concentration for all experiments was 0.8M except for 24 h which is 0.2M and the pH was 0.7, 1 and 0.7 respectively for the 24 h, 168 h and 72 h experiments. Only deionized water was used for the 24 h and 168 h experiments. Deionized and tailings water were both used for the 72 h experiment. In each experiment, the slurry was filtered and the solids were washed with deionized water.

Rare earth oxalate (RE oxalate) and rare earth hydroxide (RE hydroxide) were produced from the sulphuric acid roast of the concentrate for comparison to solids produced using organic acids. 100 g of monazite concentrate was immersed in 85 mL of 98 % sulphuric acid. Once thoroughly mixed, the sample was located in a Furnace Industries PF-62B2C-M furnace at 210 °C for 4 hours and after which the material was left to air cool. Next, the roast product was immersed in 450 mL of deionized water to solubilize the rare earth sulphate and agitated at 500 rpm for 4 h. The slurry was filtered and the solids separated from the solution. 2.5 L of deionized water was added to the leach solution and the pH was increased to 1.5 using ammonium hydroxide (30 %).

In a glass vessel, 125 mL of oxalic acid (2.1 M) was added to the monazite sulphate solution under agitation at 500 rpm for 2 h and 25 °C. The slurry was filtered and the solids were washed with deionized water. ICP-OES was used to analyse the solution and XRD was employed to characterize the samples. At this point, RE oxalates (solids) had been created. Finally, the oxalate filter cake was digested with sodium hydroxide solution (2.5M). The mixture was heated at 95°C for an hour. The solution was filtered and the solids washed with deionized water. This created RE hydroxide (solids).

4 Results and discussion

4.1 Screening tests

Cerium, lanthanum, phosphorus and iron were selected to be analysed as they represented three separate important processes. Ce and La are the rare earths in greatest concentration and thus represent the most likely to be released in significant proportions under direct RE leaching. Phosphorus is contained in all of the major rare earth-bearing minerals, the dissolution of this relative to the rare earths gives information about decomposition of the minerals and potentially reprecipitation of any components. Iron is the major impurity and well-known to be preferentially dissolved in organic acids, solubilised iron will thus speak to the selectivity of the process and indicate potential impurity levels in a larger scale process.

Different results in the release of REEs and gangue from monazite concentrate was noted under the effect of the different acids (Fig. 1). Oxalic acid demonstrated the greatest capability for solubilisation of phosphorus and iron in acidic conditions. However, these values represent

only a very small fraction of the total elements in the concentrate. None of the rare earth elements were dissolved to a significant degree. The fact that phosphorus dissolution did not appear to be directly linked to the extent of rare earth dissolution suggested multiple reactions were occurring. Most likely that either the rare earths were precipitating as another species (likely for oxalic) or the phosphorus was derived from a non-RE-bearing minerals. The low solubility of rare earth oxalates has been shown and has been used in separation and recovery process at the industrial scale (Chung et al., 1998).

From the results, it seemed likely that the chemical structure of the acid was the most important attribute for the solubilisation of phosphorus. This conclusion concurs with several studies performed by Johnston (1952; 1954a, 1954b) in the release of phosphorus in dicalcium and tricalcium phosphates. The position and number of the carboxyl groups in dicarboxylic acids are primary factors to consider (Bolan et al., 1994; Johnston & Miller, 1959; Kpomblekou & Tabatabai, 1994; Xu et al., 2004). Additional hydroxyl groups have a significant role in the solubilisation of phosphorus. This effect can be noticed between tartaric and maleic acids. Interestingly RE-citrate complexes have higher stabilities oxalates, displaying a shift from standard behaviour.

The apparent selectivity of the phosphate mineral over iron dissolution is highly interesting. Iron (III), the oxidation state believed to be present in the sample, has higher binding strengths with all four acids than rare earths and yet was dissolved to a lower degree. This may be due to a greater stability of the iron phase, poorer adsorption on the iron surface, an interaction with other components of the monazite mineral or a kinetic limitation on iron adsorption.

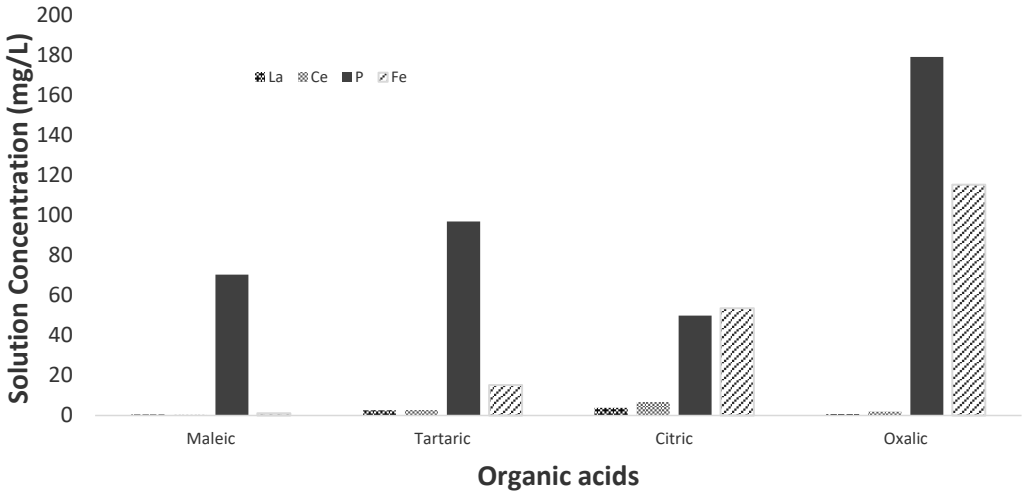

Figure 1: Leaching of monazite 0.2 M for 24 hours at pH 2 and 25°C

At pH 5 the release of all elements was lower for these reagents. This outcome might be affected by several parameters. To achieve binding or chelation, the ligand must be in contact with the surface of the mineral. It seems that some electrostatic attraction is present between the ligand and the surface of the mineral. The ligand, which is negatively charged, must bind with the trivalent rare earth element positive charge. Hence, the surface of the mineral may be negatively charged due to high pH and prevent binding with the ligand which is negatively charged. Protonation of the acid groups may be significant to the stability of the complex. It could be the impact of higher H^+ concentrations due to acidic conditions. The data currently available doesn't present a clear case for any of these being the dominant cause.

The screening experiments showed a significant solubilisation of phosphorus in more acidic conditions. Therefore, an experiment was carried out with a lower pH (pH 0.7) with the same concentration of oxalic acid (0.2M). The solubilisation of Ce and La was insignificant (pH 0.7) while the P concentration increased by a factor of 2.5 further suggesting the precipitation of a rare earth oxalate had occurred. From the point of view of the industrial scale, achieving a lower pH could be uneconomical. A pH of 1 was set for subsequent experiments.

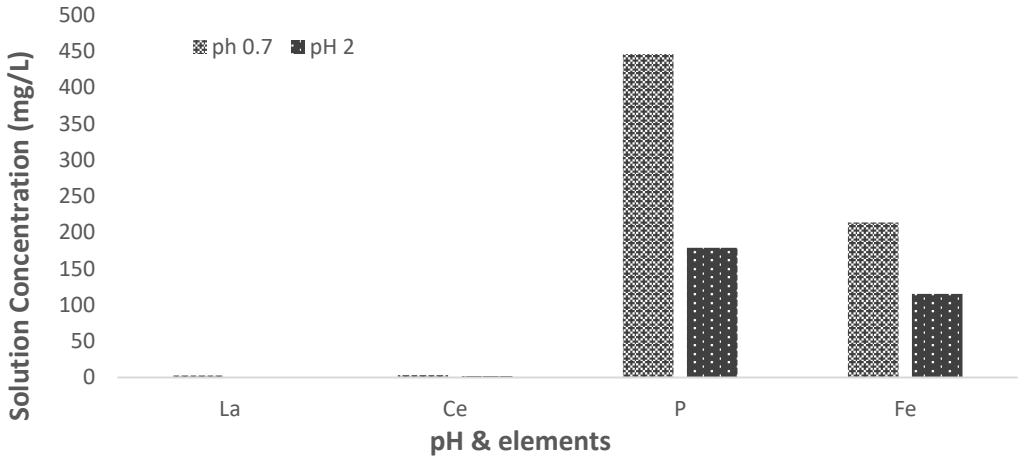

Figure 2: Leaching of monazite 0.2 M oxalic acid pH 0.7 & 2 for 24 hours.

4.2 Long term experiment (168 hours) pH 1

The leaching reaction of phosphorus and iron continued over the 168 h, with a slowly decreasing rate (fig. 3). The recovery of phosphorus and iron was approximately 27% and 3%, respectively, at 168 hours. The greater P release while maintaining very low soluble rare earth species suggests a benefit in segregating the REs from potentially recoverable impurity elements. A point of note is the decreasing release of phosphorus over time, showing a limitation on dissolution. It is possible that the reaction stopped due to oxalic acid consumption over time, however this requires further enquiry.

The change in mineralogy of the solid after oxalate leaching was analysed by XRD (fig. 4). Based on the assumption that a rare earth oxalate had been formed and the lack of that material in the diffraction database, a reference had to be produced (process defined in section 2). This was then compared to the leach residue confirming the presence of rare earth oxalates. The residue also showed decreased intensity in the monazite peaks displaying that the concentration had been reduced, displaying the conversion of the phosphate mineral.

An important part of unit process development is to ensure cohesion with preceding and subsequent operations. As the flotation concentrate was used for testing, the system combines well with previous stages. Recovery and separation of REEs is a difficult and expensive process, therefore it was imperative that a similar feed could be provided to conventional solvent extraction. Current industry practice precipitates rare earths as an oxalate and then uses strongly alkaline solutions and high temperatures to convert that material to a hydroxide. To allow for separation from impurities the rare earths were solubilised from the original leach residue by a process currently under development and the hydroxylation process was then applied to that solution. Again a reference material needed to be produced for comparison. The XRD data presented in Figure 5 displays the success of the hydroxide preparation using tailings water.

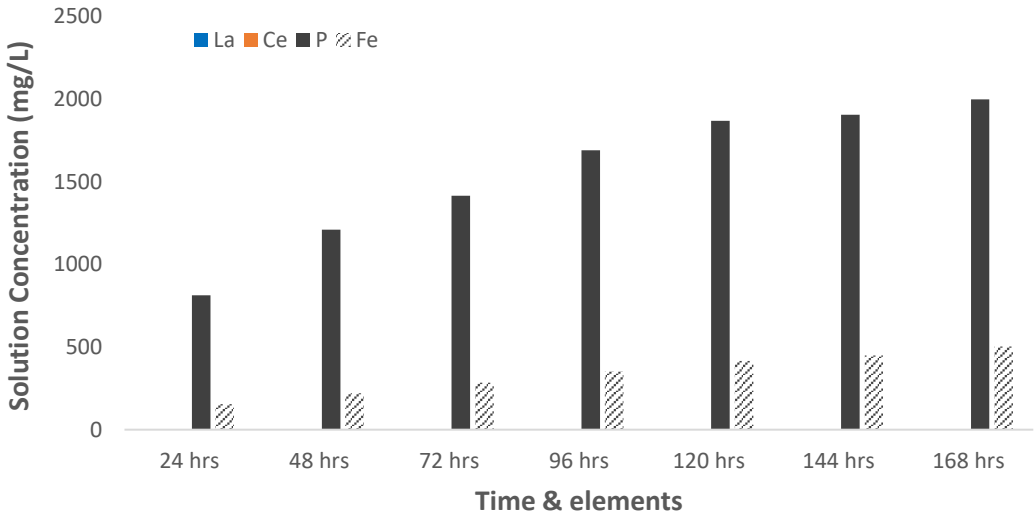

Figure 3: Leaching monazite 0.8M oxalic acid for 168 hours at pH 1 500 rpm and 25°C

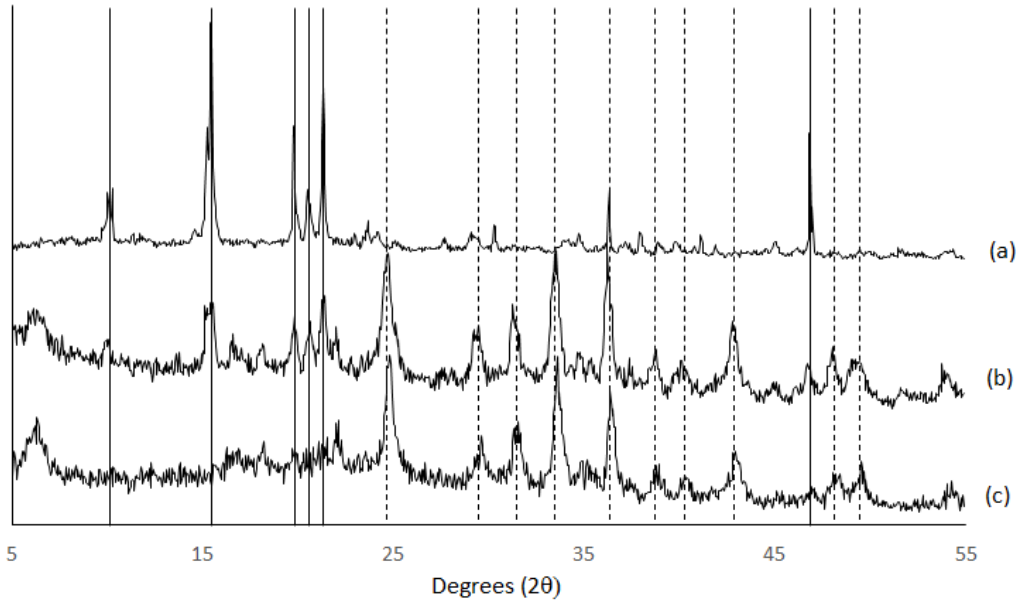

Figure 4: XRD patterns obtained from a) the rare earth oxalate produced from conventional processing, b) the residue of the oxalic leach and c) the original monazite concentrate

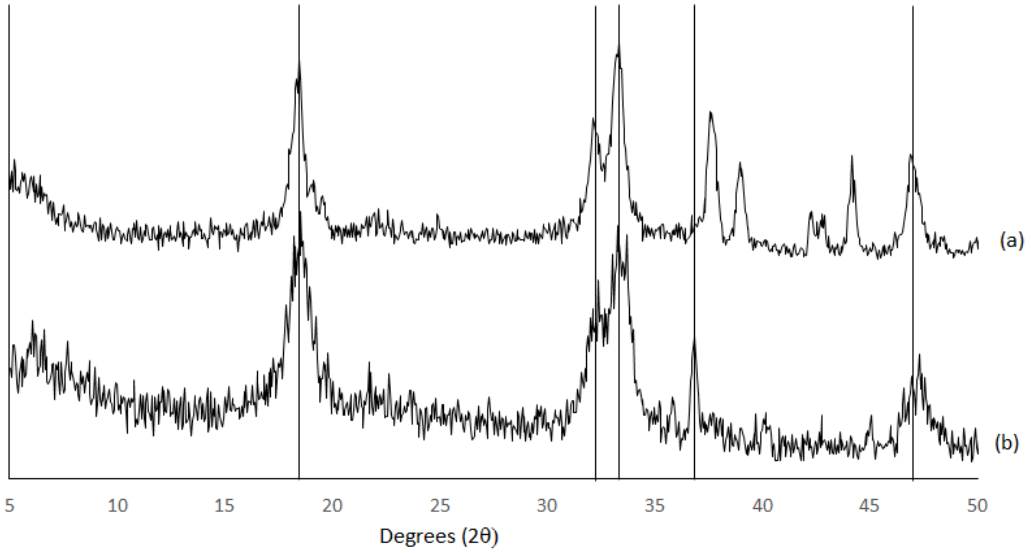

Figure 5: X-ray diffractograms of samples obtained from generation of rare earth hydroxide using tailings water a) subsequent to the secondary leach of the oxalic acid leach residue and b) from the acid roast PLS

4.3 Leaching using tailings water 72 hours pH 0.7

Monazite concentrate immersed in oxalic acid prepared in tailings water showed significant decrease in solution concentration of phosphorus, (~41 % decrease). It should be noted that there was a problem with oxalic acid solubility when trying to increase the pH to 1, therefore a lower pH was set (0.7).

The presence of significant total dissolved solids in the tailings water was identified as the main reason for the low solubility. This resulted in the desired pH (pH 1) not being achieved and the precipitation of solids. Thus, a lower pH and presence of several impurities in tailings water have a significant effect on the solubilisation of phosphorus.

The most common minerals which make water hard are calcium and magnesium. The quantity of magnesium was low (therefore, not reported in the analysis of tailings water) whereas the content of calcium was high. An insoluble calcium oxalate coating may have been created on the particle surface when the oxalic acid reacted with the calcite ($CaCO_3$) (Gierlus et al., 2012). The value of the hardness (as $CaCO_3$) was 290 mg/L, which can be classified as very hard water (more than 120 mg/L). One of the disadvantages of hard water is that calcium ions and soap molecules in water mix which result in a sticky scum that impedes soap action (Vernier Software and Technology, 2016). It is likely that the ions present in the water decreased the available oxalate in solution.

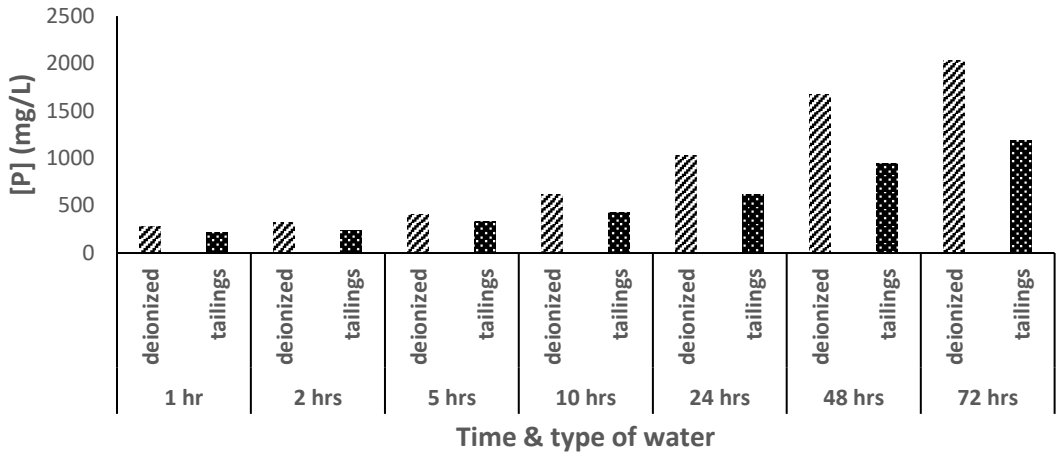

Figure 6: Comparison leaching of phosphorus in monazite 0.8 M oxalic acid for 72 hours at pH 0.7 using ionized and tailings water and 25°C

5. Summary

The type of organic acid was an important factor in the solubilisation of monazite concentrate. The degree of effectiveness of each acid relates fairly well to their ability to bind rare earths. However, citric acid has greater complex stability with rare earths than oxalic. This suggests that the reprecipitation of the oxalate is important in greater mineral dissolution. The system shows surprising selectivity to dissolve monazite over the iron phase as oxalic acid has a greater binding strength with iron than with rare earths. This may be due to other interactions with the phosphate, different stability of the specific phases (highly stable iron oxide), a kinetic limitation on iron dissolution or preferential adsorption to the monazite surface.

The conversion of monazite to rare earth oxalate appeared to succumb a rate limitation with time. This may be due to the precipitating material forming a passive layer on the surface of the monazite or consumption of the oxalate by dissolving ions. A rare earth hydroxide was able to be produced from the leach residue allowing this process to be applied to conventional solvent extraction. Tailings water used to test the impact of dissolved solids on the process showed a marked decrease in phosphorus release, suggesting a significant decrease in monazite conversion.

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